AMMONIA AND AMMONIUM COMPOUNDS

A

PRACTICAL MANUAL

for

Manufacturers,

Chemists,

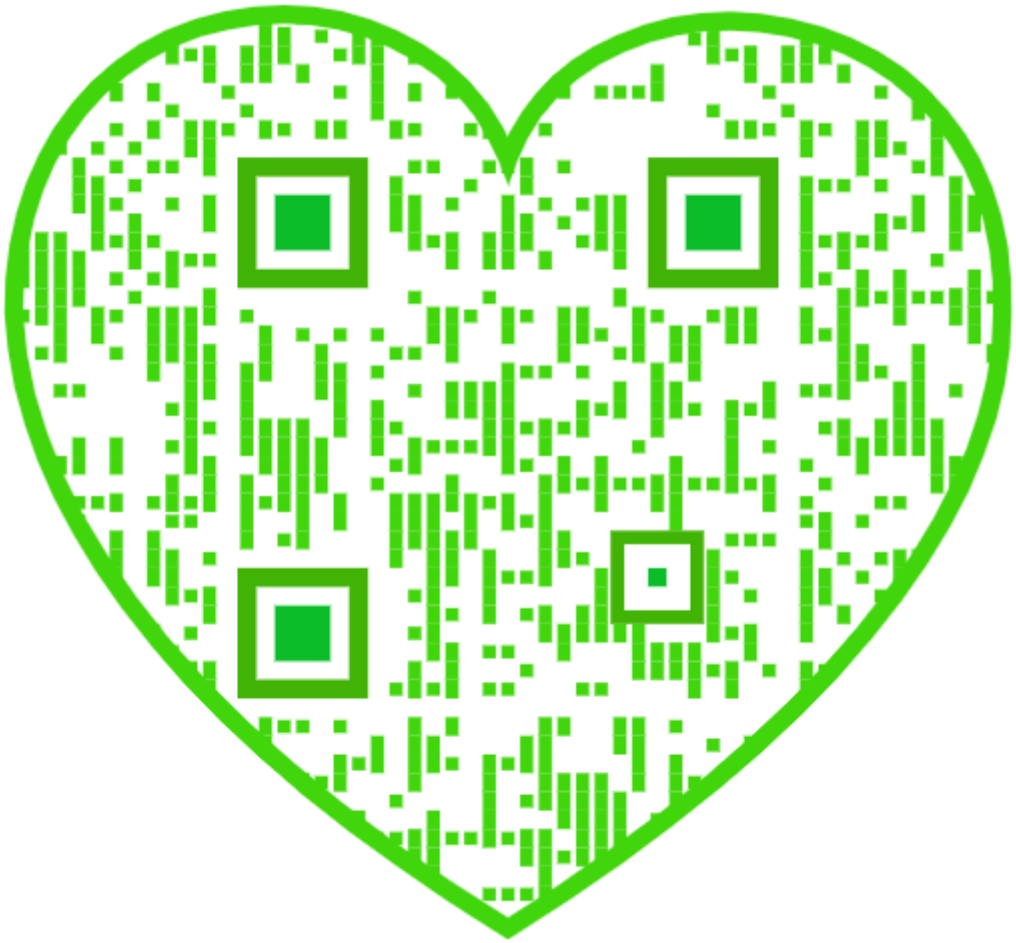
Gas Engineers,

and

Drysalters.

DR R. ARNOLD

LONDON SAMPSON LOW & CO LD



Cornell University Library

BOUGHT WITH THE INCOME
FROM THE
SAGE ENDOWMENT FUND
THE GIFT OF
Henry W. Sage
1891

A225909 5/8/08

9963

Cornell University Library
arV19178

Ammonia and ammonium compounds :

3 1924 031 273 505
olin,anx

PHILIP HARRIS & Co., Ltd.,

BIRMINGHAM,

Manufacturers and Importers of every description of

Chemical Apparatus and Chemicals for Analysis.

ALLEN'S, BUNTES', ORSAT'S, HEMPEL'S, &c.,
APPARATUS FOR GAS ANALYSIS.

STANDARD PENTANE LAMP.

HARCOURT'S COLOUR TEST APPARATUS.

SULPHUR TESTING APPARATUS.

PRESSURE GAUGES, METERS, &c.

PYROMETERS AND THERMOMETERS OF EVERY FORM.

Agents for Oertling's, Becker's, &c., Balances.
Schleicher and Schull's Rhenish, and Müncktell's
Swedish Filter Papers.

Our Illustrated Catalogue of Chemical and Physical Apparatus and Chemicals, with upwards of 1200 Illustrations, sent post free on application.

AMMONIA

AND

AMMONIUM COMPOUNDS

Comprising their Manufacture from Gas-liquor, and from Spent-oxide (with the recovery from the latter of the bye-products, Sulphur, Sulphocyanides, Prussian-blue, etc.); special attention being given to the analysis, properties, and treatment of the raw materials and final products

A PRACTICAL MANUAL FOR MANUFACTURERS, CHEMISTS, GAS-ENGINEERS, AND DRYSALTERS

FROM PERSONAL EXPERIENCE, AND INCLUDING THE MOST RECENT DISCOVERIES AND IMPROVEMENTS

BY

DR. R. ARNOLD

TRANSLATED FROM THE GERMAN BY

HAROLD G. COLMAN, PH.D., M.Sc.

ILLUSTRATED BY NUMEROUS WOODCUTS

SECOND EDITION

LONDON

SAMPSON LOW, MARSTON, SEARLE, & RIVINGTON

Limited

St. Dunstan's House

FETTER LANE, FLEET STREET, E.C.

1890

[*All rights reserved*]

LONDON:
PRINTED BY GILBERT AND RIVINGTON, LIMITED,
ST. JOHN'S HOUSE, CLERKENWELL ROAD.

PREFACE.

NOTWITHSTANDING the existence of the Handbooks of Lunge and Fehrmann, I have ventured, at the request of the publishers, to treat of the present position of the Ammonia industry in this little work. I have also found it necessary to include a description of the treatment of the "spent-oxide" from the coal-gas purification—an industry which is intimately related to the foregoing, and of which no connected description has as yet been published.

The book may therefore be regarded as an attempt to collect descriptions of all the processes necessary for the utilization of the nitrogen present in coal.

I have omitted mentioning obsolete views, even when still held by certain chemists and others, the object of the work being to portray briefly the present position of the two above-named industries, both of which are so closely connected with the coal-gas manufacture.

To remedy a want in the present literature on this subject, I have given special attention to the analysis of the final products, and also of the raw material and other substances required in the various processes. Should these methods, which are based upon practical experience, prove acceptable, a step will have been taken in the direction of unity in analytical methods, which result is greatly to be desired in this as in other industries.

In the description of the treatment of the spent-oxide many gaps will doubtless be found, owing to the difficulties which surround the task, the publications on the subject being neither numerous nor exhaustive. Moreover, the various processes employed are kept strictly secret, so that, except for the scanty literature at my disposal, I have been thrown back on my own experience.

THE AUTHOR.

October, 1888.

CONTENTS.

I. CHEMISTRY OF AMMONIA :—

PAGE

1. Ammonia 1
   a. Composition and Properties . . . 1
   b. Occurrence and Formation . . . 3

2. Ammonium Compounds 8
   a. Ammonia and Water 8
   b. Ammonium Sulphate 10
   c. „ Chloride (Sal-ammoniac) . 12
   d. „ Carbonate 13
   e. „ Sulphide 15
   f. „ Nitrate 16
   g. „ Phosphate 16
   h. „ Thiocyanate (Sulphocyanide) 16
   i. „ Oxalate 17
   k. „ Metavanadate . . 18
   l. „ Molybdate 18
   m. „ Chromate 18
   n. „ Thiosulphate (Hyposulphite) 19
   o. „ Cyanide 19

3. Detection and Estimation of Ammonia . . 20
   a. Qualitative Detection of Ammonia . 20
   b. Estimation by Distillation . . . 20
   c. „ „ the Azotometric Method . 23
   d. Preparation of Standard Solutions and Reagents 25

II. MANUFACTURE OF AMMONIUM COMPOUNDS . 28

1. Raw Material 28
   a. Gas-Liquor 28

MANUFACTURE OF AMMONIUM COMPOUNDS (*continued*).

PAGE

b. Sulphuric Acid 35
c. Lime 38
d. Hydrochloric Acid 38
e. Nitric Acid 38

2. Ammonium Sulphate 39
a. Old Methods of Manufacture . 39
b. Continuous Working Apparatus . . 41
c. Subsidiary Apparatus 46
d. Regulation of the Process . . . 48
e. Analysis of Ammonium Sulphate . . 51
f. Applications „ „ . . 52
g. Double Salts 53

3. Caustic Ammonia (Liquor Ammoniæ) . . 55
a. Manufacture 55
b. Analysis and Application . . . 61

4. Concentrated Gas-Liquor 62

5. Ammonium-Chloride or Sal-Ammoniac . . 64
a. Manufacture of Crystallized Sal-Ammoniac 64
b. Other Methods of Preparation . . 66
c. Sublimation of Sal-Ammoniac . . 68
d. Application and Valuation . . 69

6. Ammonium Carbonate 70

7. „ Nitrate 73

8. „ Thiocyanate (Sulphocyanide) . 75

9. „ Phosphate 77
a. Manufacture 77
b. Ammonium Superphosphate . . . 78

10. Ammonium Chromate. 79

11. „ Oxalate 81

12. „ Sulphide 81

13. „ Vanadate. 82

14. „ Bye-Products and Waste Products from the Gas-Liquor . 82

MANUFACTURE OF AMMONIUM COMPOUNDS (*continued*).

PAGE

a. Waste-Gases 82
b. Lime Mud 84
c. Waste-Liquor 84

III. UTILIZATION OF THE "SPENT-OXIDE" . . 86
1. Chemical Changes in the Purification of Coal-Gas by Ferric Oxide 86
a. Separation of Sulphur 86
b. Separation of Nitrogen Compounds; Composition of certain Spent-Oxides . 89
c. Revivification of the Spent-Oxide . . 92
2. Treatment of the Spent-Oxide . . . 93
a. The Raw Material 93
b. Recovery of the Thiocyanates (Sulphocyanides) 98
c. Recovery of Ferrocyanides . . . 101
d. Extraction of the Sulphur . . . 105

APPENDIX 111
1. Tables 111
2. Recent Literature 121
3. ,, Patents 124

INDEX 127

I.

CHEMISTRY OF AMMONIA.

1. Ammonia.

(*a.*) *Composition and Properties.*—Ammonia is a compound of one volume of nitrogen with three volumes of hydrogen, and is therefore represented by the chemical formula NH_3. It contains *by weight* 82·35 per cent. of nitrogen, and 17·65 per cent. of hydrogen. Its molecular weight is 17.

Ammonia gas was discovered by Priestley in 1774, and described by him under the name of "alkaline-air." Ten years later, Berthollet showed that it consisted of nitrogen and hydrogen, but its exact quantitative composition was first ascertained at the commencement of the present century. Although, however, ammonia is a comparatively recent discovery, its compound with hydrochloric acid (sal-ammoniac), was known as early as the eighth century to the Arabian alchemist Geber, and was a valuable article of commerce in the fifteenth century.

Ammonia is a colourless gas, possessing a very characteristic pungent smell. It is much lighter than air, having a specific gravity (air = 1) of 0·586, one litre of the gas weighing at the normal temperature and pressure 0·76193 grams. When strongly cooled or

subjected to great pressure, it condenses to a liquid, which boils under the ordinary pressure at — 33·7. If it be further cooled below — 75° it solidifies, forming a colourless crystalline mass, which possesses only a faint odour. If the liquid ammonia be allowed to evaporate quickly, it absorbs heat rapidly from its surroundings, a property which has been largely made use of for the preparation of artificial ice. It is extremely soluble in water, one volume of water absorbing at the ordinary temperature more than 700 volumes of the gas. The solution possesses the characteristic odour of the gas, colours red litmus paper blue, and turmeric paper brown, and possesses all the characteristic properties of an alkali.

When ammonia is passed through a red-hot tube, or is subjected to the action of the electric spark, it is resolved into its constituents ; from two volumes of ammonia, three volumes of hydrogen, and one of nitrogen are obtained. Under ordinary conditions it is incombustible, but if mixed with oxygen, it burns with a pale yellow flame.

Ammonia is especially distinguished by its property of uniting with acids. Its solution in water acts in every respect like an alkali ; it has an alkaline taste, is strongly caustic, and saponifies fats. By the addition of various acids to the solution and evaporation to dryness, ammonia salts of the acids are obtained, which are very similar to the corresponding potassium and sodium salts. Further, like caustic potash and soda, it precipitates the heavy metals from their solutions as hydroxides.

If a galvanic current be passed through mercury

and caustic soda solution in such a manner that the mercury forms the negative pole, whilst the positive pole is placed in the caustic-soda solution, sodium separates at the negative pole, and unites at once with the mercury, forming an amalgam. If a solution of ammonia be substituted for caustic soda, an amalgam is likewise obtained; it forms a light, buttery mass, which becomes crystalline at low temperatures, but rapidly decomposes into ammonia, hydrogen, and mercury.

Up to the present, the constituent of the amalgam corresponding to the sodium has not been isolated, but it has been found that it differs from ammonia by containing an additional atom of hydrogen, and is therefore represented by the formula NH_4. To this hypothetical compound the name *Ammonium* has been given.

From this, and further theoretical considerations, we are justified in regarding the compounds of ammonia with acids, as salts of the hypothetical ammonium; this assumption, moreover, shows in the clearest possible manner, the analogy between these substances and the corresponding potassium and sodium salts, as will be plainly seen from an examination of the following formula :—

Potassium chloride.	Sodium chloride.	Ammonium chloride.
KCl	$NaCl$	$(NH_4)\,Cl$
Potassium sulphate.	Sodium sulphate.	Ammonium sulphate.
K_2SO_4	Na_2SO_4	$(NH_4)_2\,SO_4$
Potassium nitrate.	Sodium nitrate.	Ammonium nitrate.
KNO_3	$NaNO_3$	$(NH_4)\,NO_3$

(*b.*) *Occurrence and Formation.*—Ammonia plays a very important part in the economy of nature. It is

invariably formed by the putrefaction of the nitrogenous constituents of plants and animals, being either given off into the atmosphere, or dissolved in running water. The atmospheric ammonia is absorbed by falling rain, and again brought to the earth's surface, and there taken up by the soil, to serve as one of the chief sources of nitrogen for the vegetable world. Although the atmosphere contains about 80 per cent. of nitrogen, the plants have not the power of absorbing it directly, and are therefore dependent on the more active nitrogen compounds, ammonia and nitric acid, for their supply of this element, which is required especially for the formation of the seeds and fruit. It seems probable, however, that the plants can only assimilate the nitrogen from nitric acid, and that the ammonia is first oxidized to that compound by some as yet unknown process which takes place in the soil. It will be seen, therefore, that ammonium compounds form, either directly or indirectly, a powerful manure, and in fact, their cheapest representative, ammonium sulphate, is employed almost solely for this purpose. Moreover the value of stable manure depends largely on the amount of ammonia which has been found in it by putrefaction.

Ammonium compounds do not occur in large quantity in nature. A thin layer of ammonium carbonate is found in the guano deposits on the West Coast of South America. Ammonium sulphate and chloride are also contained in the Tuscan "Suffioni." Sal ammoniac is further found as a sublimate in the craters of active volcanoes. None of these occurrences have, however, any technical importance. In

former times ammonium compounds were obtained almost entirely from decayed nitrogenous matter, camel's excrement being, a few centuries ago, the chief source of sal-ammoniac. Later on it was also prepared from human urine, and even at the present time ammonium salts are here and there recovered from sewage.

When nitrogenous substances of either animal or vegetable origin are subjected to the process of dry distillation, they are decomposed. Charcoal remains behind, and combustible gases, tarry matter, and ammoniacal water are evolved. For a long time substances rich in nitrogen, such as bones, horn, leather, &c., were thus distilled for the sake of the ammonium salts they yielded; at present, although these processes are still carried out, the ammonium compounds have become a merely secondary consideration, the chief object being the preparation of animal charcoal, or of potassium ferrocyanide (prussiate of potash). The quantity of ammonia obtained from these bodies forms but a very small fraction of the present production.

At the present day the dry distillation of coal, the valuable residue of a past vegetable world, forms the richest and almost inexhaustible source of ammonia.

When coal is heated in closed vessels to a temperature of 1100°—1200° C. (2000°—2200° F.) it decomposes, coal-gas, coal-tar, and ammoniacal liquor are evolved, and a more or less pure form of carbon, termed coke, remains behind. Coal contains on the average about 1 per cent. of nitrogen, but the

amount varies considerably in the different varieties, as the following table shows :—

Locality.	Percentage of Nitrogen (by weight).
Northumberland	2·21
Upper Silesia	2·00
Lancashire	1·93
S. Staffordshire	1·71
Westphalia	1·65
Ohio	1·50
Wales	1·18
Scotland	1·04
Saarbrücken	0·60
Zwickau	0·50

In the process of dry distillation only a comparatively small quantity of the nitrogen is evolved as ammonia, amounting as a general rule to 15—20 per cent.; about 30 per cent. is given off in the form of cyanides and sulphocyanides, nitrogenous compounds in the tar, and other gaseous bodies, whilst 50 per cent. remains in the coke. According to a recent statement, if steam be passed into the retorts at the close of the distillation, the yield of ammonia can be raised to 70 per cent. of the total nitrogen.

The chief purpose of the distillation of coal on the large scale is either the preparation of coal gas for lighting purposes, or the manufacture of coke. In the former case it is absolutely necessary to collect all the liquid products, whereas in the coke manufacture the condensation is frequently neglected.

The relative proportions of the products formed from 2 cwt. of coal in coal-gas manufacture and coking are given in the following table :—

	Gas liquor containing 1·5—3·0 per cent. NH_3.	Gas.	Tar.	Coke.
	Per cent.	Cubic feet.	Per cent.	Per cent.
Gas manufacture.	5—10	700—900	6—8	60—70
Coking	10—15	700—1100	2—3	75

The gas-liquor obtained from these processes has a yellow or brown colour, is mostly turbid, and smells strongly of ammonium sulphide and tarry matter. Its composition is variable, but it contains as a rule 1·5—3·0 per cent. of ammonia. This exists partly as volatile compounds (including ammonium sulphide and carbonate), and partly as non-volatile compounds, such as sulphate, chloride, thiosulphate (hyposulphite) and thiocyanate (sulphocyanide).

In the coal-gas manufacture a second ammoniacal bye-product, the so-called "spent-oxide," is obtained. After the ammonia gas has been freed from ammonia in the washers and scrubbers, it is passed over hydrated oxide of iron to absorb the sulphuretted hydrogen. When the mass ceases to absorb sulphur, it is exposed to the action of the air and frequently damped and stirred to promote oxidation. By this means the iron sulphide is reconverted into hydrated iron oxide, sulphur separating out at the same time. When the oxidation is complete, the oxide can again be employed for purification. After this process has been repeated a number of times the quantity of sulphur in the mass may rise to 40—50 per cent. Besides sulphur, however, ammonium compounds (sulphate and thiocyanate) are also deposited in quantities varying from 5—10 per cent., and frequently also very considerable quantities (5—25 per cent) of Prussian blue.

Of late years, therefore, the spent-oxide has received a large amount of attention, not only as a source of ammonium compounds, but also of ferrocyanides and thiocyanates.

The ammoniacal liquors obtained from the preparation of animal charcoal and potassium ferrocyanide have at the present time lost most of their importance, notwithstanding the fact that they are exceptionally rich in ammonia, chiefly in the form of carbonate. The liquor from bones is a brown nauseous-smelling liquid, having a density of 7—15° Tw. On distillation it always gives a yellow distillate, and cannot therefore be employed for the manufacture of colourless salts.

2. Ammonium Compounds.

(*a.*) *Ammonia and Water.*—When ammonia dissolves in water a considerable evolution of heat takes place, the volume of the solution increasing at the same time. The solubility of ammonia in water at various temperatures is given in the following table :—

One volume of water absorbs :

At 0° C. (32° F.)	...	...	1050 vols. ammonia.
„ 10° C. (50° F.)	...	...	813 „ „
„ 15° C. (59° F.)	...	...	727 „ „
„ 20° C. (68° F.)	...	...	654 „ „

100 grams of water dissolve 50—60 grams of ammonia at the ordinary temperature. The aqueous solution of ammonia comes into commerce as *caustic ammonia*, or *liquor ammoniæ*. It has a sp. gr. of 0·880—0·930 and contains from 35—20 per cent. of ammonia. If the

solution be warmed, ammonia gas is evolved ; the more concentrated the solution, the lower the temperature at which the evolution begins. If, on the other hand, it be cooled to $-40°$ white crystals separate out. When a rapid current of air is passed through a cold concentrated solution, the temperature of the liquid falls so low that mercury freezes if placed in it.

The solution is decomposed by chlorine with formation of nitrogen and hydrochloric acid. If, however, chlorine be in excess, *chloride of nitrogen* is formed. This is a yellow, extremely explosive oil which is also formed by the action of chlorine on ammonium salts.

By the action of acids on ammonia solution, or by passing ammonia gas into aqueous solutions of acids, *ammonium salts* are obtained. If the acid be replaced by its anhydride, we get instead of the salt of the corresponding acid, a so-called amido-salt. Thus, for example, by the action of ammonia on sulphuric anhydride, ammonium amidosulphonate is formed.

$$SO_3 + 2\,NH_3 = SO_2\begin{cases} NH_2 \\ ONH_4 \end{cases}$$

From ammonia and carbon dioxide again we obtain ammonium carbamate.

$$CO_2 + 2\,NH_3 = CO\begin{cases} NH_2 \\ OHN_4 \end{cases}$$

All these compounds unite with water, forming salts of the acid corresponding to the anhydride employed.

As has already been stated, the ammonium salts bear a remarkable resemblance to the corresponding

potassium and sodium compounds in their general character, such as solubility, crystalline form, &c. They are, however, distinguished from them by their instability at high temperatures, no ammonium compound being known which is not decomposed at a red heat; many of them indeed are volatile with steam, and some few evaporate even at the ordinary temperature. When heated with alkalies or alkaline earths, ammonia is at once set free, and may be easily recognized by its characteristic pungent smell. Further, all ammonium salts are decomposed by alkaline hypobromites with evolution of nitrogen.

(*b.*) *Ammonium Sulphate.*—$(NH_4)_2SO_4$. This salt is obtained by neutralizing sulphuric acid with ammonia. It separates from a hot saturated aqueous solution on cooling, in beautiful large rhombic tables, which are very readily soluble in water.

According to Alluard, 100 parts of water dissolve at

0° C.	(32° F.)	71·00 parts	$(NH_4)^2SO_4$
20° C.	(68° F.)	76·30	„ „
50° C.	(122° F.)	84·25	„ „
80° C.	(176° F.)	92·20	„ „
100° C.	(212° F.)	97·50	„ „

It melts at 140° C. (284° F.), and decomposes at a higher temperature with evolution of ammonia, and sulphur dioxide. If its solution be boiled with one of common salt, a double decomposition takes place, sodium sulphate and ammonium chloride crystalling out on cooling. When heated with calcium carbonate (chalk), ammonia and ammonium carbonate pass off, and calcium sulphate (gypsum) remains behind. The chemically pure salt finds an application in

analytical chemistry, being employed for standardizing normal-acid solutions. The sulphate prepared on the large scale is used exclusively as manure.

Ammonium sulphate combines also with other sulphates forming double salts. Of these, the most important is ammonium-alum, or aluminium ammonium sulphate.

$$Al_2(SO_4)_3(NH_4)_2SO_4 + 24\ H_2O.$$

It is obtained as a crystalline meal by mixing concentrated solutions of the two sulphates, and in all its properties closely resembles the common or potash alum. On ignition, it loses ammonia and sulphuric acid, whilst pure alumina remains behind. 100 parts of water dissolve only 12 parts of the double salt at the ordinary temperature, whereas at the boiling point, 422 parts are dissolved. At the present day, ammonium-alum is not manufactured to the same extent as in former years, when the price of potassium salts was much higher. It is chiefly used in dyeing and calico-printing.

Ferrous Ammonium Sulphate.—$FeSO_4 + (NH_4)_2 SO_4 + 6\ H_2O$ is formed when a hot saturated solution of iron vitriol is added to a similar solution of ammonium sulphate; on cooling, the double salt separates in bluish-green monoclinic crystals. It is used instead of iron vitriol in dyeing, calico-printing, and analytical chemistry, as it possesses over the latter the great advantage of undergoing no alteration in the air.

Nickel Ammonium Sulphate.—$NiSO_4 + (NH_4)_2 SO_4 + 6\ H_2O$ can be obtained in a similar manner to the foregoing salt. It crystallizes in dark-blue monoclinic

prisms, which dissolve in sixteen parts of cold, and three parts of boiling water, and is employed in nickel-plating.

Cuprammonium Sulphate.—$CuSO_4 4\,NH_3 + H_2O$ is not a true double salt. It may be regarded as copper vitriol in which four molecules of water of crystallization have been replaced by four of ammonia. A solution of copper vitriol gives with excess of ammonia a deep blue solution, which on addition of alcohol deposits the above compound in dark blue crystals. These dissolve in 1·5 parts of water, have an unpleasant metallic taste and slight ammoniacal odour.

The pure salt is employed in medicine in nervous diseases and affections of the eye, the crude substance being also employed in the preparation of coloured fireworks, and for the destruction of vermin.

(*c.*) *Ammonium Chloride* (*Sal-Ammoniac.*)—NH_4Cl. This, the first known ammonium salt, is obtained by neutralizing hydrochloric acid with ammonia.

$$NH_3 + HCl = NH_4Cl.$$

It is very soluble in water, the solubility at different temperatures being given in the following table :—

100 parts of water dissolve

at 0° C.	20° C.	40° C.	60° C.	80° C.	100° C.
28·4	37·3	46·2	55·0	63·9	72·8 parts NH_4Cl.

The saturated solution boils at 115°—116° C. (239°—241° F.).

It crystallizes from its hot solution in snow-white, feathery aggregates, which are built up of small regular octahedra. It dissolves also to some extent in alcohol. On boiling the solution, a small quantity

of ammonia is given off, and the solution becomes slightly acid, and therefore attacks iron.

Sal-ammoniac has a sharp, saline taste, and is unaltered in the air, but can be sublimed at a higher temperature. The vapours evolved consist of a mixture of free ammonia and hydrochloric acid, which reunite on cooling. If the cooling take place quickly, it forms a light, crystalline powder; if, on the other hand, the vapours are slowly cooled, a semi-transparent, fibrous, crystalline mass is obtained.

In the middle ages, sal-ammoniac was prepared from camel's excrement. Even at the present time the dried excrement forms the sole available fuel in the desert. The soot deposited on burning it, contains considerable quantities of sal-ammoniac, which may be obtained by extracting with hot water and evaporating the solution thus obtained. It was brought into commerce by Armenian merchants, and hence obtained the name *sal armeniacum*. Later on this name was changed to *sal ammoniacum*, a name which had been originally given to the common salt (sodium chloride) found near the ruins of the temple of Jupiter Ammon in the Libyan desert, and with which this *sal armeniacum* was confused. In the course of time, *sal ammoniacum* became contracted to *sal-ammoniac*, which name forms the source of the word ammonium, of which sal-ammoniac and the numerous analogous compounds are now regarded as derivatives.

Sal-ammoniac is largely used in dyeing and calico-printing, and also in brazing and soldering.

(*d.*) *Ammonium Carbonate.*—Neutral ammonium carbonate $(NH_4)_2CO_3$ is an extremely unstable body.

It forms fine silky crystals, which contain one molecule of water of crystallization, and smell strongly of ammonia. The crystals lose ammonia on standing in the air, and become opaque, forming acid ammonium carbonate.

Commercial ammonium carbonate (*sal-volatile*, or *salt of hartshorn*) is not a true carbonate. It is obtained by heating a mixture of ammonium sulphate with calcium carbonate, and consists of a mixture of acid ammonium carbonate with ammonium carbamate, $NH_4HCO_3 + CO\begin{cases}NH_2\\ONH_4\end{cases}$ free ammonia being evolved during its preparation. It is also formed when neutral ammonium carbonate is distilled.

When the salt is exposed to the air, it loses ammonia, leaving about 50 per cent. of acid ammonium carbonate. It is readily soluble in water, 4 parts of water dissolving at the ordinary temperature 1 part of the salt; the solution contains both neutral and acid salt, and on heating gives off carbonic acid at 75° C. (167° F.), ammonia at 85° C. (185° F.) and at 100° C. (212° F.) the whole is volatilized.

If sal-volatile be dissolved in concentrated ammonia solution, crystalline plates of normal ammonium carbonate are obtained. On treating with alcohol, ammonium carbonate goes into solution, whilst the acid carbonate remains undissolved.

Acid Ammonium Carbonate.—NH_4HCO_3 is usually prepared from sal-volatile by allowing it to stand in the air, or by passing carbonic acid through its saturated aqueous solution. It forms small crystalline plates, which dissolve in 7—8 parts of water. It

occurs in crystalline and fairly pure condition in the lower layers of the guano deposits in South America.

Ammonium Carbamate.—$CO\left\{\begin{matrix}NH_2\\ ONH_4\end{matrix}\right.$ is deposited as a white saline mass, when dry carbonic acid and ammonia are brought together. It smells strongly of ammonia, and volatilizes at 60° C. (140° F.). It is converted by water into ammonium carbonate.

(*e.*) *Ammonium Sulphide.*—$(NH_4)_2S$ is obtained as a white crystalline mass when one volume of sulphuretted hydrogen and two volumes of ammonia gas are brought together.

$$2NH_3 + H_2S = \left.\begin{matrix}NH_4\\ NH_4\end{matrix}\right\}S.$$

It is easily soluble in water, is somewhat volatile at the ordinary temperature and loses ammonia in the air, forming

Ammonium Hydrosulphide.—$\left.\begin{matrix}NH_4\\ H\end{matrix}\right\}S$. This can also be prepared by saturating a solution of ammonia with sulphuretted hydrogen. Like the foregoing compound, it is easily soluble, and undergoes alteration in the air. It occurs in gas-liquor, often in considerable quantity.

Higher ammonium sulphides, such as $(NH_4)_2S_4$ and $(NH_4)_2S_5$ are obtained by the action of sulphur on ammonium sulphide solution. A mixture of these bodies was formerly used in medicine under the name "volatile liver of sulphur."

Ammonium Hydrosulphide is largely used in analytical chemistry, but none of these compounds

have much technical importance. The hydrosulphide is occasionally used for the purpose of etching copper.

(*f.*) *Ammonium Nitrate.*—NH_4NO_3. To prepare this salt, nitric acid is neutralized with ammonia or ammonium carbonate. It forms, colourless, rhombic crystals, which are somewhat hygroscopic, and dissolve at the ordinary temperature in half their weight of water. By its solution a considerable absorption of heat takes place, the temperature of the liquid being consequently lowered. It is also readily soluble in alcohol. It melts at 152° C. (305° F.), and when heated beyond this point, splits up into nitrous oxide and water.

$$NH_4NO_3 = N_2O + 2H_2O.$$

Nitrous oxide or "laughing-gas" is largely used by dentists as an anæsthetic agent.

(*g.*) *Ammonium Phosphate.*—Common phosphoric acid forms three ammonium salts, viz :—*Normal Ammonium Phosphate* $(NH_4)_3PO_4$ *Hydrogen Ammonium Phosphate* $(NH_4)_2HPO_4$, and *Dihydrogen Ammonium Phosphate* $(NH_4)H_2PO_4$. The first two salts are rather unstable, losing ammonia in the air and leaving a residue of Dihydrogen ammonium phosphate. This salt can be easily prepared from phosphoric acid and ammonia in the ordinary manner. It crystallizes in colourless quadratic prisms, similar to those of the corresponding potassium salt. It dissolves easily in water, giving a solution which has an acid reaction.

(*h.*) *Ammonium Thiocyanate or Sulphocyanide.*—

NH_4CNS has of late years assumed some technical importance. It is often contained in considerable quantities in *spent-oxide*, from which it is now recovered on the large scale, and also occurs in gas-liquor in varying quantities. English gas-liquors may contain as much as 1 per cent., but as a general rule the amount does not exceed 2—3 grm. per litre.

Ammonium thiocyanate can also be obtained by heating ammonium thiocarbonate to 100 C. (212° F.)

$$CS\begin{cases}NH_2\\SNH_4\end{cases}=NH_4.CNS + H_2S.$$

The latter body is obtained by the action of carbon-bisulphide on an alcoholic solution of ammonia.

$$CS_2 + 2NH_3 = CS\begin{cases}NH_2\\SNH_4.\end{cases}$$

The yield is, however, by no means good.

According to Gélis, ammonium sulphide and carbon bisulphide combine together to form ammonium thiocarbonate $(NH_4)_2CS_3$, which, on heating, likewise splits up into ammonium thiocyanate and sulphuretted hydrogen. It may, moreover, be obtained by the action of hydrocyanic acid on yellow ammonium sulphide.

The salt is very easily soluble in water and alcohol, and crystallizes in large colourless deliquescent plates which are somewhat volatile with steam. It melts at 159° C. (318° F.) and decomposes on further heating.

(*z.*) *Ammonium Oxalate.* The neutral salt $\begin{cases}CO_2NH_4\\CO_2NH_4\end{cases}$ is obtained by saturating a solution of oxalic acid with ammonia, and crystallizes with one molecule of

water in long rhombic prisms. It is easily soluble in water, insoluble in alcohol, and on heating loses water, forming oxamide $\begin{cases} CO.NH_2 \\ CO.NH_2. \end{cases}$ The acid salt $\begin{cases} CO_2NH_4 \\ CO_2H \end{cases}$ is obtained by adding to a solution of oxalic acid one half the quantity of ammonia necessary for its complete saturation. It crystallizes in needles which also contain one molecule of water, and is less soluble than the normal salt. On heating it loses water and is converted into oxamic acid $\begin{cases} CO.NH_2 \\ CO_2H. \end{cases}$

(*k.*) *Ammonium Metavanadate.*—NH_4VO_3 forms a white crystalline powder, which is very sparingly soluble in water, almost insoluble in sal-ammoniac solution, and completely insoluble in alcohol. On heating, it loses ammonia, leaving a residue of vanadic anhydride. The solution of the salt gives with tincture of galls, a deep black ink, which is, however, according to Wöhler, not permanent. The vanadate is employed in the preparation of aniline black.

(*l.*) *Ammonium Molybdate.*—$(NH_4)_2Mo.O_4$ is obtained as a white powder by neutralizing molybdic acid with ammonia and precipitating the salt by addition of alcohol. If the solution be evaporated ammonium heptamolybdate $(NH_4)Mo_7O_{24} + 4H_2O$ is obtained. The solution of this salt in nitric acid is employed for the detection and estimation of phosphoric acid.

(*m.*) *Ammonium Chromate.*—$(NH_4)_2CrO$ is pre-

pared by saturating a solution of chromic acid with ammonia. It crystallizes in yellow needles which are permanent in the air. On ignition it loses ammonia and oxygen, and is converted into chromium sesquioxide.

Ammonium Dichromate.—$(NH_4)_2Cr_2O_7$ which crystallizes in large red crystals, is prepared by adding the requisite quantity of chromium trioxide to the normal salt. Ammonium chromate is employed in calico printing.

(*n.*) *Ammonium Thiosulphate or Hyposulphite.*—$3(NH_4)_2S_2O_3 + H_2O$ crystallizes in beautiful tables which are permanent in the air. It is formed by the oxidation of ammonium sulphide in the air, and is converted by stronger oxidizing agents into ammonium sulphate. On addition of acids sulphur-dioxide is evolved, and sulphur separates. It is found in considerable quantities in gas-liquor.

(*o.*) *Ammonium Cyanide.*—NH_4CN is prepared by saturating hydrocyanic acid with ammonia, or by distilling a mixture of potassium ferrocyanide and sal-ammoniac. It is also formed when gaseous ammonia is passed over red-hot charcoal.

$$2NH_3 + C = NH_4CN + H_2$$

It is a white deliquescent salt, smelling strongly of ammonia and hydrocyanic acid; it volatilizes at 36° C. (97° F.), the vapour being combustible, and extremely poisonous. It is also very soluble in alcohol, and undergoes oxidation in the air, assuming a brown colour. Like the foregoing salt, it is found in gas-liquor.

3. Detection and Estimation of Ammonia.

The qualitative detection of ammonia presents no difficulty. All ammonium compounds when heated with caustic soda solution evolve ammonia, which is easily recognized by its characteristic pungent odour. If a piece of red litmus paper be placed in the vapour, it at once becomes blue, the colour again changing to red on exposure to the air for a short time, through the evaporation of the ammonia. Further, if a glass rod, moistened with dilute hydrochloric acid, be brought in contact with the gas, thick white fumes of sal-ammoniac are formed.

On the addition of platinum chloride to a fairly concentrated solution of an ammonium salt, a yellow precipitate of ammonium platini-chloride $(NH_4)_2 PtCl_6$ is formed. Tartaric acid likewise gives a white crystalline precipitate of acid ammonium tartrate.

Ammonia can be detected in extremely small quantities by means of the solution known as "Nessler's reagent," which consists of an alkaline solution of mercuric chloride in potassium iodide. This gives with solutions containing ammonia, a reddish brown precipitate, or if the solution be very dilute a similar coloration. The latter is still perceptible when the solution only contains 0·000001 per cent. of ammonia.

For the quantitative determination of ammonia two methods are at present in common use, viz. the distillation, and the azotometric method.

(*b.*) *Estimation of Ammonia by Distillation.*—In

this process, a certain quantity of ammoniacal liquor or of ammonium salt is distilled with a solution of caustic soda, and the vapour given off passed into a measured quantity of normal acid. Instead of caustic soda, other alkalies or alkaline earths, such as caustic potash, lime, baryta, or magnesia, may be employed to drive off the ammonia. Magnesia differs from the other agents, inasmuch as it does not decompose the sulphocyanates and amido-salts with evolution of ammonia, and on this account it has been proposed in various quarters to use only magnesia in the valuation of ammonia liquors. As, however, in the actual working lime is invariably employed, it seems more rational to employ the same agent, or the more convenient and similarly acting caustic soda. In making an estimation of ammonia in gas-liquor apart from the sulphocyanates and amido-salts, it is of course necessary to employ magnesia. For the analysis of ammonium salts which are free from these impurities it is a matter of indifference which of the above substances is employed.

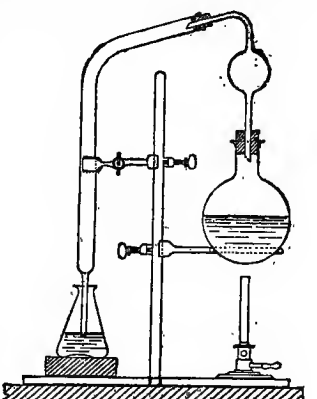


Fig. 1.

Fig. 1. shows a simple and convenient form of distilling apparatus for this process. The substance in which the ammonia is to be estimated is mixed with caustic soda solution in the flask; the vapours which are given off on boiling pass through the exit tube,

the bulb on which serves to keep back any particles of liquid which may be carried along with the vapour. The latter then passes through the wide tube into a flask or beaker containing the normal acid. The width of this tube should be such that in case of the liquid being sucked back none of it can be drawn into the distilling flask. For the examples given in the following paragraphs, (but for these only) the capacity of the tube should be about 300 cc. and that of the beaker or flask about 200 cc.

For the analysis of ammonium sulphate, for example, 10 grams of a good average sample are taken and dissolved in 500 cc. of water, 50 cc. of this solution then mixed with caustic soda, and the vapours passed into 20 cc. of normal acid. At the end of the distillation, the acid is titrated back with normal caustic soda solution. Let us suppose that 5 cc. of the latter are required for neutralization, then 15 cc of acid have been saturated. The quantity of ammonia evolved from 1 gram of ammonium sulphate amounts therefore to $0{\cdot}017 \times 15 = 0{\cdot}255$ grams. (1 cc. normal acid corresponds to 0·017 grams ammonia.) From these numbers it follows that the salt contains 25·5 per cent. NH_3.

To determine the quantity of ammonia in a gas-liquor, 10 cc. are distilled with caustic soda, and the vapour again passed into 20 cc. normal acid. Let us suppose that 6 cc. of normal caustic soda solution must be added to neutralize; then the quantity of ammonia is $14 \times 0{,}017 \times 10 = 2{\cdot}38$ per cent. The time required for an estimation is from half to three-quarters of an hour.

(*c.*) *The Azotometric Method* depends upon the decomposition which all ammonium salts undergo on treatment with alkaline hypobromites, the whole of the nitrogen being set free. The reaction which takes place is represented by the following equation :—

$$3\ NaBrO + 2\ NH_3 = 3\ NaBr + 3\ H_2O + N_2.$$

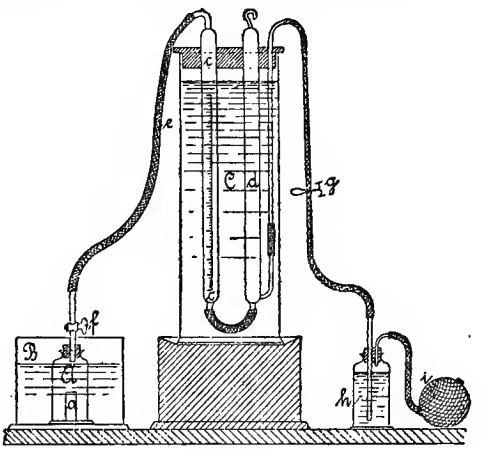


Fig. 2.

In the analytical process, a known quantity of the ammoniacal solution is mixed with a solution of bromine in caustic soda, and the nitrogen evolved collected and measured.

The most convenient apparatus for the purpose is Knop's Azotometer, as improved by Wagner,[1] which is represented in Fig. 2.

[1] This apparatus can be obtained from C. Gerhardt, Bonn, price 34*s*.

A is a bottle, to the bottom of which a tube *a* of 20 cc. capacity is fused. *B* is a glass vessel filled with water. *C* is a large cylinder, likewise filled with water, in the cover of which are fixed the graduated burette *c*, and a corresponding tube *d*, the two tubes being connected at the bottom. A side tube is also fused into *d*, and combined by the indiarubber tube *g* with the bottle *h*. By pressing the indiarubber ball *i*, water can be forced into *c* and *d*.

In carrying out an estimation, 10 cc. of the ammonia solution (which may be diluted, if necessary) are placed in the tube *a*, and about 50 cc. of sodium hypobromite solution placed in the large bottle *A*. The stopper is then pushed tightly in, and the bottle placed in the cooling vessel *B*, the three-way-cock *f* being so placed that *A* is in connection with the air. As soon as *A* and *B* have the same temperature, *f* is turned so as to connect *A* with the burette *c*, which has in the meantime been filled with water to the zero point. The liquids in *A* and *a* are now carefully mixed by inclining the bottle, and then vigorously shaken. Part of the water in *d* must previously be let off to allow room for the nitrogen which is given off. After the completion of the reaction, time is allowed for the whole to attain a constant temperature, and then the water in *c* and *d* brought to the same level, and the volume of nitrogen read off. The volume thus found must be reduced in the usual manner to the volume at 0°C. and 760 mm., and its weight in milligrams calculated. To convert the weight of nitrogen thus found into ammonia, it is necessary to multiply by $\frac{17}{14} = 1{\cdot}214$.

The analyses performed by the azotometer are quickly performed, and sufficiently accurate.

(*d.*) *Preparation of the Standard Solutions and Re-agents.*—For the preparation of the standard acid and alkaline solutions it is best to employ sulphuric acid and caustic soda. Normal oxalic acid should not be employed, as its strength is not constant, decomposition gradually taking place on standing. If normal hydrochloric acid be employed, there is always a possibility of loss taking place during the process of distillation ; for, although the normal acid may be heated to the boiling point without losing any hydrochloric acid, it must be remembered that the lower part of the delivery tube sometimes becomes sufficiently hot to evaporate any of the acid with which it is moistened, thus causing a small loss.

Standard baryta-water can only be obtained as a decinormal solution, and is therefore never employed, for in the ammonia industry such a dilution is superfluous, normal and seminormal solutions being sufficiently accurate. The use of Fleischner's seminormal ammonia is likewise inadvisable, as it constantly loses strength, even when the burettes are connected by india-rubber tubing to the bottles containing the re-agents. In the latter case loss of ammonia may take place from evaporation through the india-rubber tubes employed, as the author has had frequent opportunities of observing. Moreover, it is impossible to titrate seminormal ammonia with acid without loss of ammonia taking place, although in the reverse process—titration of acid with seminormal ammonia —the loss may be practically disregarded.

For the purpose of standardizing, the best substance is ammonium sulphate, because it is readily obtained in the pure state by neutralizing pure sulphuric acid with ammonia.

The preparation of the normal sulphuric acid and caustic soda solutions is carried out in the following manner. 50 grams sulphuric acid of 170° Tw. are diluted to 1 litre, and 160 grams of caustic soda solution, of 1·27 sp. gr., and free from carbonate diluted to the same amount. 20 cc. of the acid are then titrated with the alkali, to obtain their strength relatively to one another. 1 gram of pure ammonium sulphate, dried at 110°C. (230° F.) is next distilled with dilute caustic soda, and the vapours evolved passed into 20 cc. of the acid, and this then titrated, and the quantity of acid saturated calculated. Let us assume that the amount found is 15 cc. The acid is in that case too strong, as 1 gram of ammonium sulphate corresponds exactly to 15·15 cc. of normal acid. To 1 litre of the acid must therefore be added $\frac{(15{\cdot}15-15)\ 1000}{15} = 10$ cc. water. The corrected acid is then again compared with the caustic soda solution, and the above process repeated, until it is found that the acid is exactly normal. The caustic soda solution is then diluted, so as to correspond exactly, volume for volume, with the acid.

The normal solutions must be kept in well-stoppered bottles, so that no change of strength can take place from evaporation, or absorption of carbonic acid. When a large number of titrations have to be made in succession, it is preferable to

connect the burettes with the bottles containing the acid and alkali by means of glass and indiarubber tubing.

Tincture of Litmus.—100 grams Litmus are digested for some time with 500—600 cc. water, and the solution after filtering divided into two equal parts. To one of these a few grains of salicylic acid are added, and then sufficient sulphuric acid to colour it distinctly red, after which both portions are again united.

Methyl-orange Solution.—To prepare this solution 1 gram methyl-orange is dissolved in a litre of water.

Sodium Hypobromite Solution.—80 grams of caustic soda (free from nitrogen) are dissolved in water, and diluted to rather less than a litre. To the well-cooled solution 20 cc. of bromine are then gradually added, and sufficient water to make the whole to 1 litre.

Nessler's Re-agent.—25 grams corrosive sublimate, and 50 grams potassium iodide are separately dissolved in water, and then mixed together. To the filtered solution, 150 grams of caustic soda solution of sp. gr. 1·2 — 1·3 (free from ammonia) are added, and the whole diluted to one litre.

II.

MANUFACTURE OF AMMONIUM SALTS.

1. Raw Materials.

(*a.*) *Gas-liquor.*—This may practically be regarded as the sole source of ammonia at the present time. The preparation of ammonium compounds by the distillation of animal matter, which was formerly so flourishing, has now become quite insignificant. The *spent-oxide*, which contains considerable quantities of ammonium salts, must be regarded as a source of sulphur and of cyanides, rather than of ammonia, the latter being in that case a bye-product. To this subject a special chapter is devoted later on.

Chemical Composition, and Methods of Analysis.—As has already been stated, the ammonia in gas-liquor does not exist in the free state, but combined with various acids. Some of these compounds are volatile with steam, and others not. The composition of the gas-liquor is extremely variable, as the following analyses will show :—

(1) Analysis of Leeds gas-liquor (S. Dyson) :—

Total Ammonia	. . . . .	20·45	grams per litre.
„ Sulphur	. . . . .	3·92	„ „
Ammonium Sulphide	NH_4HS . .	3·03	„ „
„	Carbonate $(NH_4)_2CO_3$ . .	39·16	„ „
„	Chloride	14·23	„ „
„	Thiocyanate . . .	1·80	„ „
„	Sulphate	0·19	„ „
„	Thiosulphate . . .	2·80	„ „
„	Ferrocyanide . . .	0.41	„ „

(2) Analysis of an English gas-liquor by two chemists (Kay and Appleyard) :—

	Kay.	Appleyard
Total Ammonia . . .	2·91 %	2·98 %
Volatile „ . . .	2·72 „	2·64 „
Ammonium Thiocyanate .	0·17 „	0·16 „
Total Sulphur . . .	0·638 „	0·636 „
Ammonium Sulphide NH_4HS	0·936 „	0·901 „
„ Sulphite . .	0·156 „	0·152 „
„ Chloride . .	1·05 „	1·03 „
„ Sulphate . .	0·013 „	0·013 „
„ Thiosulphate .	trace	trace
„ Ferrocyanide .	0·947 „	0·948 „

The sp. gr. of this gas-liquor at 16° C. (61° F.) was 1·035 (7° Tw.).

Gerlach gives the following table of the composition of various German gas-liquors :—

Constituents (in grams per litre).	Chemnitz.	?	Bonn.	Trier.	Zurich.
Total Ammonia	12·09	9·40	18·12	15·23	3·47
Ammonium Thiosulphate	1·036	·628	5·032	2·072	0·296
Ammonium Sulphide	0·340	0 646	6·222	2·468	1·428
Ammonium Carbonate	1·050	1·470	2·450	} 33·763	5·856
Acid Ammonium Carbonate	4·560	7·680	33·120		
Ammonium Sulphate	0·462	0·858	1·320	} 4·922	1·926
Ammonium Chloride	30·495 (?)	17 120	3·745		

From these tables the great variation in the composition of gas-liquors is very apparent. This difference does not depend merely on the coal employed, but also very largely upon the method of working, and on special local circumstances.

For the valuation of gas-liquors, the usual plan adopted in England is to determine the number of

ounces of pure sulphuric acid (H_2SO_4), necessary to saturate one gallon of the liquor. For this purpose 16½ oz. of best rectified oil of vitriol (= 16 oz. pure H_2SO_4) are diluted with water to one gallon. The sp. gr. of this solution should be 1·068 at 15° C. (60° F.). This acid is then run into 16 liquid ounces of gas-liquor until the solution is neutral to litmus paper. The quantity of dilute acid used corresponds to the number of ounces of pure H_2SO_4 necessary to neutralize a gallon of gas-liquor. This test only indicates the amount of volatile ammonia.

Frequently the strength of gas-liquor is simply estimated by its density, as given by Twaddell's hydrometer. In place of this, Fleischner's densimeter is frequently employed. In the latter, the specific gravity is obtained directly by placing the figure I and the decimal point before the number of degrees recorded. Thus, 50 degrees on the densimeter correspond to a sp. gr. of 1·50.

All hydrometer measurements must be made at the temperature for which the instrument is graduated (generally 60° F.) In cases where it is impossible to bring the liquor to this temperature, a correction must be made, which should be experimentally determined once for all.

As a general rule the higher the density of a gas-liquor, the larger is the amount of ammonia it contains. It is generally assumed that each degree Twaddell corresponds to two ounces of sulphuric acid. It is, however, manifest that with a liquid having such a varying composition as gas-liquor, the results obtained by measurement of the density will often

differ very considerably from those given by analysis. If the accurate composition is required, it is therefore necessary to perform a complete analysis.

The method of estimating the total ammonia in gas-liquor has already been given (p. 22). In works where there is no proper laboratory, the following method, proposed by Knublauch, may be employed. The gas-liquor, after being diluted with four times its volume of water, is shaken with an excess of lime. The filtrate, which contains all the ammonia and a certain quantity of dissolved lime, is neutralized with acid of known strength, and from this the quantity of ammonia calculated, correction being made for the amount of acid required to neutralize the dissolved lime. The analysis is actually carried out as follows: 100 cc. gas liquor are diluted with water to 500 cc., and shaken with an excess of quicklime, and allowed to stand for an hour. After filtering, 50 cc. of the filtrate are taken, a little aurine added as an indicator, and the solution titrated with acid. Knublauch has constructed a special cylinder for this purpose, from which the acid is allowed to drop into the liquid. If the acid be of the given strength, and filled to the zero mark on the cylinder before each determination, the percentage of ammonia can be directly read off on the cylinder after the titration.

By this method results are obtained which are accurate to 0·1—0·2 per cent.

For a complete analysis of gas-liquor, S. Dyson[1] recommends the following method :—

[1] Journ. Soc. Chem. Ind., 1883, p. 231.

Total Ammonia.—25 cc. gas-liquor are distilled with magnesia.

Carbonic Acid.—50 cc. gas-liquor are precipitated with calcium chloride solution, the precipitate filtered, washed, and dissolved in normal acid. The excess of acid is titrated back with alkali.

Total Sulphur.—25 cc. gas-liquor are treated with hydrochloric acid containing bromine. The excess of bromine is evaporated off, and after filtration the boiling solution precipitated with barium chloride.

Sulphur in the form of Sulphide.—A portion of the gas-liquor is precipitated with zinc sulphate and ammonium chloride. The precipitate is filtered off, dissolved in hydrochloric acid containing bromine, and the solution precipitated as before with barium chloride.

Sulphuric Acid.—250 cc. gas liquor are evaporated to dryness, the residue taken up and treated with zinc oxide to remove ammonium sulphide, and the filtered solution precipitated with barium chloride.

Thiosulphuric, or Hyposulphurous Acid is calculated from the difference between the total sulphur on the one hand, and the amount of sulphur in the form of sulphide, sulphate, and thiocyanate (sulphocyanide).

Chlorine.—50 cc. gas-liquor are evaporated, the residue dissolved in water, and the filtered solution precipitated with a mixture of copper sulphate and iron vitriol, and again filtered. The filtrate is then acidified with nitric acid, and precipitated with silver nitrate.

Ferrocyanic Acid.—250 cc. are evaporated, and the residue dissolved in water and precipitated with ferric

chloride. The precipitate is then filtered, washed decomposed with caustic soda, and the residual oxide of iron collected and weighed.

Thiocyanic or Sulphocyanic Acid.—50 cc. are evaporated and the residue heated to 100° C. (212°F.) for four hours, extracted with alcohol, the alcoholic solution filtered off, and the alcohol evaporated. The residue is dissolved in water and precipitated with a solution of copper sulphate containing sulphurous acid. The precipitate is filtered off and then dissolved in nitric acid and reprecipitated by caustic soda.

Thiocarbonic Acid is separated by means of zinc sulphate, the precipitated zinc salt being washed with cold water. On boiling with water this salt is decomposed, forming carbon bisulphide, which may be estimated by means of the compound which it forms with methylphosphine.

Carriage and Storage.—In cases where the gas-liquor is not worked up at the place of manufacture, it is conveyed to the works either in iron boiler-shaped railway trucks holding about ten tons, in canal boats, or in specially constructed waggons.

For the purpose of storage it is best to employ wrought-iron tanks, which are placed either level with the ground or in elevated positions. The former serve for the general storage of the liquor, whilst the latter are employed to feed the stills, both systems being connected together by iron pumps.

The best form for the lower tanks is that of a horizontal cylindrical boiler, these being the cheapest both in construction and in setting up. Where possible, the tanks should not be sunk below the level of the

floor, as in that case leaks may long exist unobserved, and repairs are difficult and tedious to execute. For the upper tanks vertical cylinders of the same height and diameter are employed, as horizontal tanks would be too costly in fixing.

In smaller works, reservoirs of wood are frequently met with ; these remain tight for a long time provided that they are always kept full. The cost of erection is much the same as for the iron reservoirs.

Gas-liquor gradually attacks iron, the action being especially due to the cyanides, sulphocyanides and sulphides it contains, which form with it ammonium ferrocyanide and iron sulphide. On this account, reservoirs of cement have of late been frequently employed in place of the iron ones, and so far as can at present be learned, these answer the purpose very well. In several quarters Monnier's cement reservoirs have been recommended. These are made from a skeleton of wire network of the required shape by coating it on both sides with cement. Their cost is only half that of iron tanks, and they have the additional advantage of being very light, the thickness of the walls being only about two inches. A reservoir holding 500 cubic feet costs approximately *22l.* 10*s.*

A process has recently been patented by Kunheim for the removal of ammonium sulphide from gas-liquor, previous to its employment in the manufacture of ammonium salts. It consists in passing a very strong finely divided stream of air through the cold liquor, which carries all ammonium sulphide along with it, the mixed gases passing through dilute alkali

containing iron hydroxide in suspension. The iron sulphide formed is at once reconverted by the air into iron hydroxide, the sulphur separating out in the free state. As yet it is unknown whether any practical application of the process has been made. The separation of sulphuretted hydrogen from the gas-liquor before distillation would be of great advantage in many cases, especially for the preparation of sal-ammoniac. It has frequently been proposed to precipitate the sulphur by means of iron, or other metallic salts, but this has always proved too costly.

Before distillation the gas-liquor must of course be allowed to settle well, and should be quite clear. If it still contains tarry matters in suspension, there is no likelihood of obtaining colourless products.

(*b.*) *Sulphuric Acid.*—Three varieties of Sulphuric Acid are brought into commerce. (1) Acid of 106° Tw. or 1·5 sp. gr., containing 60 per cent. H_2SO_4. (2) Acid of 142° Tw. or 1·76 sp. gr., containing 78 per cent. H_2SO_4. (3) Acid of 168° Tw. or 1·83 sp. gr., containing 92—93 per cent. H_2SO_4.

For the preparation of ammonium sulphate, the second variety, (142° Tw.) is usually employed. It is a colourless, odourless, oily liquid, mostly rather cloudy from the presence of lead sulphate.

The valuation of sulphuric acid is almost invariably performed by taking its density with Twaddell's Hydrometer, or by the above-mentioned densimeter. From the specific gravity the percentage of sulphuric acid can at once be found by means of the table given in the Appendix.

In taking the density the following precautions must be observed :—(1) The cylinder in which the test is performed must be quite dry ; (2) The acid must not be allowed to stand for any length of time in contact with the air ; (3) The temperature of the acid during the operation must be 15° C. (60° F.) unless the hydrometer is graduated for a different temperature ; (4) Especial care must be observed that the sample is not taken from the surface of the liquid, but from the bottom by means of a siphon.

If the acid is not abnormally impure (which is ascertained by a qualitative examination described later) the results obtained from the determination of its density are quite as accurate as those found by titration. To perform the latter operation about one gram of the acid is weighed out in a stoppered flask, diluted with water, and titrated with normal alkali solution. It should be noted that strong sulphuric acid cannot be measured by means of a pipette without considerable error, on account of the oily nature of the liquid.

The impurities usually occurring in commercial sulphuric acid are arsenic, iron, lead, aluminium, and also sulphurous, nitrous, and nitric acids. The non-volatile impurities are determined by evaporating 1—2 grams of the acid in a platinum dish, igniting and weighing the residue. This should not amount to more than 0·5 per cent. Nitrous and nitric acids are detected by the iron sulphate test. This consists in carefully pouring a solution of ferrous sulphate into the sulphuric acid in a test tube. If either of the two acids named are present, a dark ring is formed where the two layers came in contact. The presence of

sulphurous acid is shown by adding pure zinc to the acid. If the hydrogen evolved also contain sulphuretted hydrogen,—which is recognized by its property of blackening lead acetate paper,—then sulphurous acid is present. To detect arsenic, the acid is diluted with its own volume of water, and bright copper foil placed in the liquid. In presence of arsenic this assumes a steel-grey colour.

For the transport of sulphuric acid, glass carboys containing 17—20 gallons are almost invariably employed in this country. It has frequently been proposed to carry it in iron tanks, but this method has not been used to any great extent in England. In Germany, on the other hand, these tanks, mounted on railway trucks, are largely used. So far as convenience and safety in loading, transit, and unloading are concerned, there is no comparison between the two methods. The men engaged in loading and unloading the carboys must always be specially protected in case of accident, whereas the tanks are easily filled and emptied by means of an air pump.

The tanks in question are constructed of strong iron plate, and provided with a man-hole, delivery tap and pump. Only the upper portions of the tank, which frequently come in contact with the air, need to be protected by lead, for at the ordinary temperature strong sulphuric acid has no action on iron in absence of air.

In the works the acid is stored in covered rectangular troughs, coated with lead on the inside. The acid is conveyed from these to the place required by means of lead tubes, in which cast-iron taps or plugs are inserted.

(*c.*) *Lime.* This substance is of great importance as on its action the recovery of the non-volatile ammonia entirely depends. Unfortunately the lime which comes into commerce is of very varying quality.

Good lime, when moistened with a sufficient quantity of water, quickly becomes hot, swells up considerably, and falls to fine white powder.

The chemical analysis of lime gives very reliable results. For this purpose, a good average sample is finely powdered, and exactly 0·5 gram distilled with an excess of ammonium sulphate solution, the vapours being passed into 20 cc. of normal acid. At the close of the operation, the acid is titrated back, the amount of acid neutralized thus obtained.

Assuming that 16 cc. of acid were neutralized, then, as 1 cc. acid corresponds to 0·028 grams CaO, the original lime contained 16+0·028 grams = 0·448 grams or 89·6 per cent. CaO.

(*d.*) *Hydrochloric Acid.* The hydrochloric acid of commerce, such as is used in the manufacture of sal-ammoniac, has a density of 32·4° Tw., and contains about 30 per cent. HCl.

As in the case of sulphuric acid, its strength is ascertained simply by means of the hydrometer. From the specific gravity observed, the strength is calculated by the table given in the Appendix.

The usual impurities of commercial hydrochloric acid are sulphurous and sulphuric acids, chlorine, iron, arsenic, &c. It is stored and transported exclusively in glass carboys containing 17—20 gallons.

(*e.*) *Nitric Acid.* Common nitric acid is a yellowish fuming liquid of 88° Tw. or 1·44 sp. gr., containing

74 per cent. HNO_3. The coloration is due to the presence of lower oxides of nitrogen. A stronger acid of 100°—106° Tw. and 1·50—1·52 sp. gr. also occurs in commerce as "fuming nitric acid."

The valuation of nitric acid is also performed by determining its density, and calculating the strength from the table in the Appendix.

Good nitric acid should only become slightly cloudy with silver nitrate or barium chloride; when heated in a flask on the water bath, only small quantities of red fumes should be evolved. The amount of nitrous acid present may be determined by titration with standard potassium permanganate solution. It has been proved by R. Hirsch, and by Jackson and Wing, that an admixture of nitrous acid considerably *raises* the sp. gr. of nitric acid. Thus if the acid is bought simply from its sp. gr., a considerable loss may occur, an impurity of 1 per cent. of nitrous acid lowering its value by 4·6 per cent.

Storage and transport the same as with hydrochloric acid.

2. Ammonium Sulphate.

(*Ammonium Sulfuricum, Sulphate of Ammonia.*)

(*a.*) *Former Methods of Preparation.*—Ammonium sulphate is prepared by saturating sulphuric acid with ammonia, the latter being obtained by boiling any ammoniacal solution with lime.

It was formerly obtained in England by saturating the raw gas-liquor directly with sulphuric acid, and evaporating the neutral solution thus formed. Con-

centrated sulphuric acid was poured into gas-liquor until the yellow solution became milky, and this then evaporated until the salt crystallized out. The salt thus obtained was generally coloured yellow or grey, and frequently also red or blue, and contained besides ammonium sulphate other ammonium salts, such as the sulphite, chloride, and especially sulphocyanide. As sulphate free from the latter impurity commands a much higher price, this method of working has now been given up. The fact that the evaporation of the dilute salt solution consumes considerable quantities of fuel, has also assisted to this end.

To obtain the ammonia from gas-liquor the latter is treated in special stills. These are constructed so as to distil off first the volatile ammonium compounds, and then, by addition of lime and further heating, to recover the ammonia which is present in the non-volatile condition.

The apparatus formerly used was extremely primitive, consisting mostly of an ordinary directly fired boiler. After boiling until all the volatile compounds had distilled over, lime was added, and the distillation continued. Frequently indeed the last part of the process was neglected, and the non-volatile ammonia allowed to run to waste. Boilers heated by direct fire were found to wear out very rapidly, chiefly owing to the formation of a hard incrustation of lime, and the first improvement made was the employment of either open or indirect steam, i.e. blowing steam directly into, or passing it through coils placed in the liquor. Moreover, instead of

using a single boiler, a combination of two or more was made, the system being so arranged that the volatile compounds were driven off in a boiler placed at a higher level, by means of steam from a lower boiler in which the treatment with lime took place; as soon as all the ammonia was driven off from the lower boiler, it was emptied, and the liquor from the higher boiler run into it, and there treated with lime, the steam evolved being passed into the freshly filled boiler above.

The stills proposed by Rose, Mallet, Lunge, Grünewald and Wunder, are all more or less different combinations of boilers.

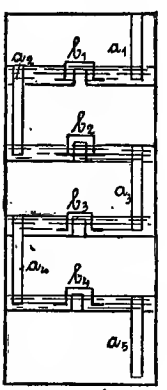


Fig 3.

(*b.*) *Continuous Working Stills.*—At the present time, no one with an exact knowledge of the ammonia-industry would erect one of the above stills. The great advances which have been made in the construction of stills in other chemical industries, especially in the process of rectifying spirits, have exerted a beneficial influence on the ammonia industry.

It is to a Frenchman, Savalle, that we owe the idea on which all modern continuous stills are based. Fig. 3 shows a portion of Savalle's apparatus. It is a vertical column divided horizontally into a number of chambers. The liquid to be distilled passes gradually downwards from chamber to chamber, by means of the overflow tubes *a*. A strong current of steam is blown in at the bottom of

the column, and passes upwards through the perforated caps *b*. These cause the steam to blow through the liquid in each chamber, and thus, as all the liquid passes in turn through each of these compartments, it must by the time it reaches the bottom have been very thoroughly boiled. Moreover this arrangement has the advantage that the fresh gas-liquor, entering at the top of the column, encounters the steam which already contains large quantities of ammonia, and as it passes downwards, constantly becoming poorer in ammonia, always meets steam which contains still less, to which it gives up another portion; until at last after undergoing the final treatment with fresh steam, it leaves the apparatus entirely freed from its volatile ammonium compounds. We have thus a current of steam mixed with large quantities of ammonia, continuously passing away from the top of the column, whilst the liquid free from ammonia flows off at the bottom, likewise in a continuous stream. This cannot be claimed even for the very best kinds of boiler-stills. In these, during the latter portion of the process, the steam passing off contains but little ammonia, and the boiling must be continued for hours, wasting immense quantities of steam, unless 0·2—0·3 per cent. of the ammonia are allowed to pass off with the waste-liquor. The columnar stills are therefore not only regular and continuous, but are also markedly economical.

The number of continuous working stills is not at present large; and here only two of these, both of which have stood the test of experience, will be

described; viz. those of Feldmann, and of Grüneberg and Blum.

Feldmann's apparatus is represented in Fig. 4.

A is the main column, *B* the vessel in which the liquor is treated with lime, and *C* the subsidiary column. The gas-liquor flows from the reservoir *a*,

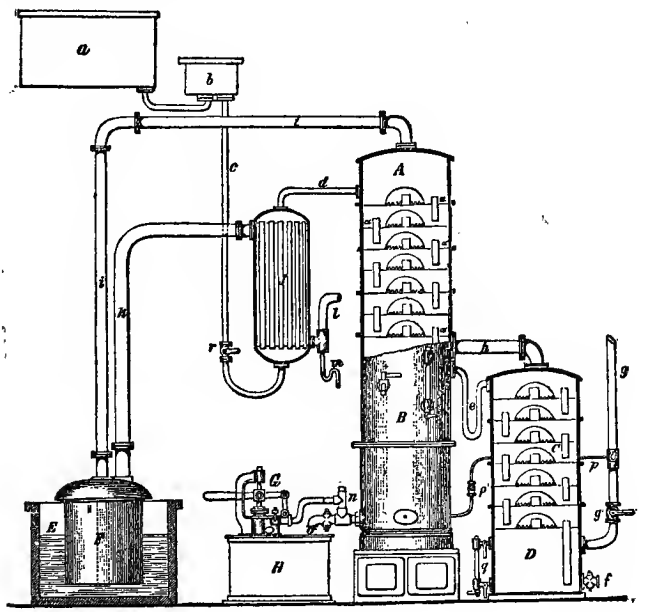


Fig. 4.

into the supply tank *b*, and thence by the tube *c* through the tubular heating apparatus *I*, to the topmost chamber of the main column. From here it flows downwards from chamber to chamber through the tubes *a*, until at last, freed from volatile ammonia, it reaches the decomposition tank *B*. By means of

the pump *G*, milk of lime is introduced into this tank at certain intervals, its contents being kept in continual agitation by passing into it through *p*, a small current of live steam. By this treatment, the non-volatile ammonium compounds are completely decomposed, and the liquor then passes through the overflow tube *e* into the subsidiary column *C*, where the ammonia which has been set free is completely driven off. The spent-liquor collects in *D* and flows away continuously through the tap *f*. The steam required for the process enters the apparatus in the lowest chamber of the column *C*, and, after passing through all its chambers, reaches the lowest chamber of the main column *A*, by means of the tube *h*. After passing through each chamber, in the usual manner, it leaves *A* by the tube *i*, charged with the accumulated ammonia, from which it is freed by passing through sulphuric acid in the apparatus *E* (described later on). The unabsorbed aqueous vapour, mixed with the carbonic acid and sulphuretted hydrogen which are set free are conveyed through *l* into the apparatus *I* (termed the economizer), where they give up a large portion of their heat to the gas-liquor passing through the tubes on its way to the column *A*. This apparatus, therefore, serves the double purpose of cooling the waste gases and heating the gas-liquor. The gases pass from here into the nearest convenient chimney.

As soon as the sulphuric acid in *E* is nearly saturated, the ammonium sulphate commences to separate out at the bottom of the vessel in the form of small crystals. These are extracted by copper spoons,

and fresh sulphuric acid added to replace the amount thus neutralized.

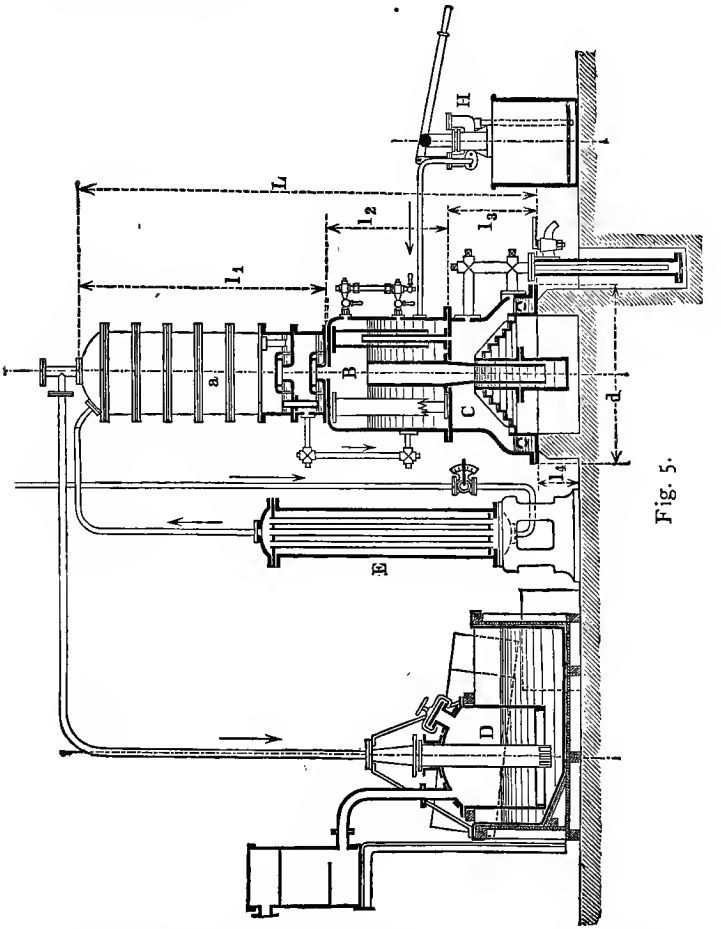


Fig. 5.

Feldmann's apparatus is now in use in a large number of gas and chemical works, and up to the

present none but favourable reports have been published. The largest stills can treat no less than 44,000 gallons in twenty-four hours. According to Feldmann's statement, for every 200 gallons of gas-liquor distilled in twenty-four hours, a boiler-heating surface of about five square feet is required.

Grüneberg and Blum's still is represented in Fig. 5.

The main portion of the apparatus consists of three essential parts; the column *a* in which the volatile ammonia is driven off, the tank *B*, in which the fixed ammonium compounds are decomposed and expelled, and the boiler *C* in which, by means of a steam coil, the last portions of the ammonia are driven off.

The gas-liquor before entering the column *a* passes through the economizer *E*, which is heated either by direct steam or by the waste gases. It then flows from chamber to chamber in the usual manner, until it reaches the lime decomposition tank, from which it passes into the boiler *C*. In this, as shown in the figure, there is a peculiar stepped cone, over the steps of which the liquor flows; in consequence of the increased area of each step, the layer of liquor in flowing downwards becomes thinner and thinner, thus permitting the passing steam to act on it very thoroughly, and to expel the last traces of ammonia. The milk of lime is introduced into *B* by means of the pump *H*.

The continuous stills are constructed of cast iron. Copper and brass must never be employed, as ammoniacal aqueous vapour quickly corrodes all metals containing copper.

(*c.*) *Subsidiary Apparatus.*—The apparatus em-

ployed for the absorption of the ammoniacal vapours by sulphuric acid, termed the *saturator*, is constructed either of wood or iron lined internally with lead, or of stone, with a leaden, bell-shaped cover. The latter construction is more generally employed.

Formerly it was the practice to use closed chambers constructed of wood and lined internally with lead, an exit tube being provided for the waste gases. In these, dilute sulphuric acid was placed, and

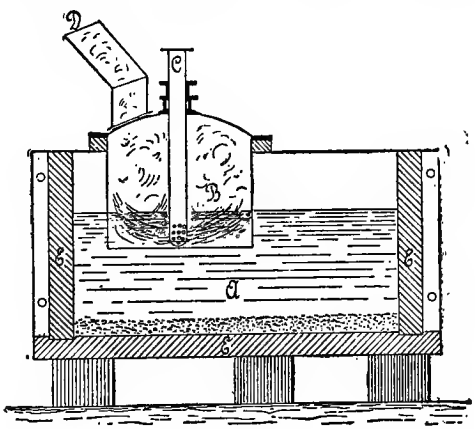


Fig. 6.

saturated with ammonia, and the solution thus obtained evaporated to the point of crystallization. This method of working has now been given up.

In Fig. 6, a modern saturator is represented. The walls *E* of the outer-chamber *A* are constructed of granite, the slabs being cemented together by sulphur and glass powder.

The bell *B* is constructed of type metal. The am-

monia tube *C*, the exit tube for waste gases *D*, are made of lead. After the waste gases have been cooled by passing through the economizer, cast iron or earthen pipes may be substituted for those of lead.

After the crystals have been extracted, they are thrown into draining chambers or on to draining boards. The former, which are constructed of wood, are made conical at the bottom, and lined with lead; the liquid which gradually trickles down passes out through a slit made in the bottom of the apparatus. The draining boards are likewise lined with lead, and are generally placed in such a position that the liquid which drops from the salt flows directly back into the saturator.

As soon as the greater part of the liquid has drained from the salt, and the latter also sufficiently cooled, it is thrown on to a stone floor coated with asphalt, so built that there is a slight fall from both sides to a central channel in which the remaining liquid collects, and is thence conveyed back to the saturator. It is of course understood that no *hot* salt solution must flow into this asphalted channel, as in that case the asphalt would become soft, and the whole coating be speedily destroyed. After lying in this manner for several days the salt contains only 4—5 per cent. of water, and is frequently brought into commerce in this condition. In other cases it is spread out in layers in heated and well-ventilated chambers, by which means the quantity of water is reduced to 2—3 per cent.

(*d.*) *Regulation of the Process.*—The regulation of the process in the manufacture of ammonium

sulphate is very simple where the mechanical arrangements are good. The stills, when once set to work, continue to work uninterruptedly, and it is only necessary to regulate the ammonia pump according to the steam pressure; to keep such a quantity of steam blowing through the still, that the waste-liquor passes off free from ammonia, which can be at once ascertained from its smell; further to pump the requisite quantity of milk of lime into the decomposition tank at the right time, to add fresh acid to the saturator to compensate for the salt extracted. In no case should *too much* steam be blown in, as all excess causes unnecessary expense; the tubes through which the ammonia passes from the still to the saturator, should never be allowed to become cold, as otherwise they may easily get blocked by condensation of ammonium carbonate, which forms an extremely hard deposit.

The quantity of sulphuric acid to be placed in the saturator depends upon the percentage of ammonia in the gas-liquor. It is very rarely necessary to place the whole of the acid required in the saturator at once. The amount to be put in each time is best ascertained by experience. When the acid is nearly saturated, the salt separates out, and then is the best time to add fresh acid.

When the process is proceeding regularly, it never happens that a liquid is obtained in the saturator which requires further evaporation. So much heat is set free by the combination of ammonia and sulphuric acid, that the liquid under the bell is kept in a continual state of ebullition, and no condensation of

aqueous vapour takes place. On the other hand, sufficient *evaporation* frequently takes place to necessitate the acid being somewhat diluted with water.

The lime should always be added in the correct proportion. This depends upon the quantity of non-volatile ammonium compounds in the gas-liquor. Ordinary gas-liquor of 4·5° Tw. requires for every 100 gallons, 6—7 lbs. of good fresh lime, or 8 lbs. slaked lime. The addition of 7—8 lbs. for each 100 gallons, is quite sufficient under ordinary circumstances.

The requisite quantity of sulphuric acid of 142° Tw. (containing 78 per cent. pure H_2SO_4) is four times the quantity of ammonia contained in the gas-liquor. Thus, in case a gas-liquor containing 2 per cent. of ammonia were being distilled, the requisite quantity of sulphuric acid would be about 80 lbs. for every 100 gallons of liquor. The amount of ammonium sulphate obtained does not differ greatly from the quantity of acid employed.

The *chemical control* consists chiefly in the examination of the raw material (gas-liquor, sulphuric acid, and lime) and of the waste-liquor. The estimation of ammonia in gas-liquor, and the valuation of lime and sulphuric acid have already been fully described.

For the examination of the waste liquor, 100 cc. are distilled with a small quantity of quicklime, and the vapours passed into 5 cc. of normal acid and the excess of acid determined by titration. Supposing that it is found that 0·5 cc. of acid have been saturated then as 1 cc. corresponds to 0·017 grams NH, the waste liquor must contain 0·5 + 0·017 = 0·0085 per cent. of ammonia.

(*e.*) *Analysis of Ammonium Sulphate.*—Especial care must be taken in obtaining a sample for analysis. It must be taken quickly, intimately mixed, and then immediately placed in a well-stoppered vessel, so that no loss of moisture takes place.

For commercial purposes the amount of nitrogen it contains is determined preferably by the distillation method (p. 21).

The salt is almost invariably sent out in somewhat damp condition, and very rarely comes into commerce quite dry. On this account it is also necessary to determine the quantity of moisture it contains. A weighed quantity of the salt is heated to 110° C. (230° F.) for several hours in a flat dish, and then again weighed, the loss of weight representing the water contained in the original salt.

For the estimation of sulphuric acid the solution prepared for the estimation of the ammonia may be employed. 50 cc. of this solution (corresponding to 1 gram salt) are acidified with hydrochloric acid, and heated to the boiling point in a beaker. To this an excess of boiling barium chloride solution is added, and the resulting precipitate allowed to settle. The liquid is then filtered, the precipitate well washed with hot water, dried, and ignited in a weighed platinum crucible to which the air is allowed access. The weight of barium sulphate thus obtained must be multiplied by $\frac{98}{233}$ to obtain the weight of sulphuric acid (H_2SO_4) in 1 gram of ammonium sulphate.

The commercial salt should have a neutral reaction. It is, however, in general slightly acid, as, in order to avoid loss of ammonia, the liquid in the saturator is

never allowed to become quite neutral. The amount of free acid is determined by titration with one-fifth normal alkali (methyl-orange or Congo-red as indicator). If 50 cc. of the ammonium sulphate solution are taken (10 grams to 500 cc.), then each one-tenth cc. of alkali used corresponds to 0·098 per cent of free sulphuric acid.

(*f.*) *Applications of Ammonium Sulphate.*—This salt is almost entirely employed as an artificial manure, being used in large quantities for agricultural purposes. It has, however, a very powerful rival, viz. Chili saltpetre, which has become very much cheaper since the "Saltpetre War" between Peru and Chili, by which Chili obtained possession of the chief export harbours. The freights from these ports to Europe being also extremely low, the competition between the two compounds has become very keen. In March, 1889, the price of ammonium sulphate was 12*s.* per cwt., whilst that of Chili saltpetre was 11*s.* per cwt. Ammonium sulphate contains about 20 per cent. of nitrogen, and Chili saltpetre 16 per cent. A hundredweight of nitrogen in the form of ammonium sulphate costs 3*l.*, whereas in the form of Chili saltpetre it costs 3*l.* 9*s.* Many agriculturists prefer to add the necessary nitrogen in the form of saltpetre, as it is supposed to act more quickly, and because moreover they appear to have a groundless preference for the foreign product. It often happens, therefore, that ammonia-nitrogen obtains a lower price than saltpetre-nitrogen, and all attempts to increase the employment of the former have been as yet unsuccessful. The profits obtained by gas-works from the

gas-liquor have therefore greatly decreased, and only large manufacturers, who can obtain sulphuric acid cheaply and work in a rational manner, get satisfactory pecuniary results. The keen competition between the two salts is very plainly shown in the following table, which gives the import of ammonium sulphate and of Chili saltpetre into Germany from 1880—1886:—

Year.	Ammonium Sulphate.		Chili Saltpetre.	
	Import in tons.	Appr ximate value.	Import in tons.	Approximate value.
		£		£
1880	33.783	675,650	55.078	853.700
1881	34,652	710,350	89,950	1,349,250
1882	34,147	717,100	126.949	1,650.400
1883	27,904	488,350	166,185	1,328,050
1884	35,967	539,500	200.647	2,006,450
1885	35.070	394.550	156.738	1,567,400
1886	36,558	420,400	181,115	1,130 500

(*g.*) *Double Salts.*—Several of the double salts of ammonium sulphate have a practical application and are manufactured on the large scale (see p. 11).

Ferrous Ammonium Sulphate is prepared by dissolving 140 lbs. of iron vitriol in the smallest possible quantity of warm water, acidifying, and allowing the solution to stand for several hours with scrap iron, and then adding a warm saturated solution of 66 pounds of ammonium sulphate. The mixture is stirred until it is cold, when the double salt separates as a bluish-green crystalline powder. This is spread out on draining boards, and dried by allowing it to stand for several days in the air.

Ferrous ammonium sulphate absorbs oxygen from the air much more slowly than iron vitriol, and may be kept for a long time without undergoing alteration.

It is employed in photography, dyeing, and in analytical chemistry.

Nickel Ammonium Sulphate is obtained by precipitating a saturated solution of nickel sulphate with a similar solution of ammonium sulphate. It forms a crystalline powder, which is washed with cold water, and recrystallized from the hot liquid. It is the most suitable salt for nickel-plating, and is largely used for this purpose.

Cuprammonium Sulphate.—For the preparation of the pure crystalline compound, copper vitriol is dissolved in caustic ammonia until cupric hydroxide begins to separate; this precipitate is then dissolved by further addition of ammonia, and an excess of methylated spirits added. Under these conditions the double salt separates gradually in dark blue crystals. These are employed in medicine for affections of the eyes and nerves.

The crude solution of this salt, obtained by the simple addition of ammonia to a solution of copper vitriol, also occurs in commerce, and is employed for destroying mildew on vines. It will probably be further employed in the future for the extinction of tree-lice, and as a disinfecting solution.

Ammonium-Alum was formerly manufactured in large quantities. Since the discovery of the Stassfurt deposits, and the consequent fall in price of potassium salts, its manufacture has been practically given up, and will therefore not be described here.

3. Caustic Ammonia.

(*Liquor Ammoniæ, or Spirit of Hartshorn.*)

(*a.*) *Manufacture.*—Until recently the aqueous solution of ammonia, or caustic ammonia, was obtained by the distillation of an ammonium salt with milk of lime. This process is now, however, given up as being much too costly, and the solution is prepared directly from gas-liquor.

Instead of distilling off first the volatile ammonium compounds, and then treating with lime to decompose the non-volatile ammonium compounds, as in the manufacture of sulphate, it is necessary in this case to add lime at the commencement of the process. By this means the ammonia vapours are obtained free from carbonic acid, but not, unfortunately, entirely free from sulphur, for the sulphide of calcium which is first formed by the action of lime on ammonium sulphide, is partially decomposed on boiling in aqueous solution, with evolution of sulphuretted hydrogen.

The continuous stills are also employed for the manufacture of this product, and are especially valuable because, when combined with a good dephlegmator or cooler, they yield an ammoniacal gas nearly free from aqueous vapour.

The crude gas thus obtained contains besides sulphuretted hydrogen, pyridine bases and other volatile constituents of tar. In order to eliminate these products the gas is first passed through a simple lime-washer, and then through a small washer containing iron hydroxide in suspension; it is also sufficient to employ a single washer containing

a mixture of these two compounds. After this the gas passes through two smaller scrubbers filled with wood-charcoal or coke, then through a washer containing concentrated caustic soda solution, and finally passes into water contained in a well-cooled saturator. Two saturators should always be employed, so that when the water in the one is nearly saturated, the gas can be turned at once into the other. The ammonia which is not absorbed in the saturators is retained by passing it through a washer containing dilute sulphuric acid. A steam pipe is connected to each of the washers and charcoal filters, by which means all the ammonia they contain can be driven off before refilling.

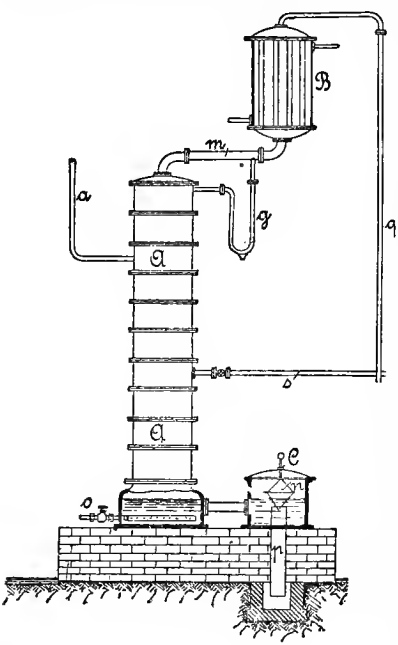


Fig. 7.

Fig. 7 shows the arrangement of the still and dephlegmator for the preparation of caustic ammonia. The gas-liquor is mixed with lime in a vessel of known size, the bottom of which is provided with a sieve, to prevent the larger pieces of lime, &c.,

passing away with the liquor. The mixture passes by means of the tube *a* (Fig. 7) into the column *A*, which is constructed exactly according to the plan shown in Fig. 3. Steam is blown in by the tube *o*, and forced upwards through the gas-liquor. The ammoniacal vapours leave the column by the pipe *m* and pass into the dephlegmator *B*. This contains a system of parallel tubes which are kept cool by water. The vapours passing through these tubes, become concentrated from the condensation of the steam, so that the ammonia gas leaves the apparatus mixed with only a small quantity of aqueous vapour, whilst the water formed by condensation passes back into the column by the tube *g*. The waste-liquor passes out through the regulator *c*, and the pipe *p* into the drain. The object of the regulator is to enable sufficient pressure to be kept up at the bottom of the column to overcome the various resistances which the gas meets in the column, dephlegmator, and washing apparatus. The liquor can only flow away from *c* when the hollow body *m* swims, which occurs when *c* and the lowest chamber of the column are filled to a certain level with water. On this account the steam can never pass away by the pipe *p*, and the necessary pressure in the column can be got up and maintained.

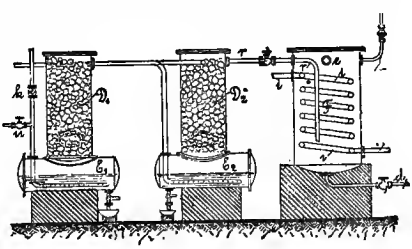


Fig. 8.

In Fig. 8 the apparatus for washing and purifying the gas is shown. The latter, after leaving the dephlegmator, passes into the washer *E*, which contains a mixture of slacked lime and iron hydroxide (bog iron ore) suspended in water. The gas, thus freed from sulphuretted hydrogen, streams upwards through the cylindrical tower *D*, which is filled with wood charcoal, and serves to restrain any liquid particles or tarry matters mechanically carried along with the gas. From *D*, the gas passes into the washer E_2, which is filled with a concentrated solution of caustic soda. This washer has likewise a small scrubber containing charcoal attached, which completely filters and purifies the ammonia gas, and allows it to pass by the pipe *r* into the saturator *F*. This is filled with pure water, which is introduced from a reservoir by the pipe *b*. After saturation, the caustic ammonia is let off through *d* into the vessels in which it is stored. To keep the liquid cool during the process of saturation, a stream of cold water is continuously passed through the coil *i*. Towards the end of the operation the whole of the ammonia is no longer absorbed, and streams through the tube *e* into a second similarly constructed saturator, which is in its turn connected with a washer containing dilute sulphuric acid, which effectually hinders any loss of ammonia.

In order to avoid interruptions it is preferable to employ a double set of purifying apparatus. As soon as the purifying agents cease to work properly, (which is at once evident from the condition of the liquor ammoniæ formed,) the reserve washers are

filled and the gas passed through them. The valves R and r are now closed, and steam passed through the washers by opening the steam valve u; instead of passing away through r into the saturator, the vapours are led from the top of D_2 by a special pipe back to the still (pipe s in Fig. 7). The end of the operation is determined by the absence of any ammoniacal smell in the vapours given off, which is easily ascertained by opening a small tap placed for this purpose in the pipe s. The vessels are then emptied. If a duplicate set of purifying apparatus be dispensed with, the pipe s is of course unnecessary.

In case it is necessary to stop the whole apparatus, the supply of gas-liquor is cut off, and the steam allowed to blow through until all the ammonia is driven out of the still and purifiers. The saturator F is in this case emptied and the ammonia absorbed solely by the acid washer.

The shape of the washers should be such that the increase of pressure caused is as small as possible. On that account a horizontal washer is represented in Fig. 8. The pressure which the ammonia gas has to overcome in such washers is so small in comparison with the other resistances that it may be practically neglected. The fact that the apparatus there sketched is very compact and easily inspected also tells greatly in its favour.

For the construction of the apparatus, cast and wrought iron are solely employed. The saturators are, however, frequently lined with lead, as it is supposed that caustic ammonia may become yellow in iron vessels. *Pure* caustic ammonia can, however,

certainly be kept in iron vessels without undergoing change, and well-purified ammonia gas may also be absorbed without danger in iron saturators.

The regulation of the process is not so simple as in the case of the sulphate manufacture. An active, careful, and conscientious foreman is required, who must see especially that the still works properly and economically. The ammonia-gas must leave the apparatus free from carbonic acid, and should only contain small quantities of aqueous vapour; the purifiers must be refilled at the proper time, so that they perform their work properly, and the saturators must never become hot. The waste-liquor must not smell of ammonia, nor show on analysis the presence of more than 0·01 per cent. NH_3.

The amount of lime to be added depends in this case on the total ammonia in the gas-liquor. As a general rule, in every 100 gals. of gas-liquor 18 lbs. of lime should be added for each 1 per cent. by weight of ammonia that it contains. The lime is slaked with sufficient water to form a thick milk, and added in this form to the gas-liquor in the reservoir. The latter is, as already mentioned, provided with a sieve at the bottom, to prevent the larger pieces of lime and other impurities passing into the still, where they might easily cause stoppages.

Dr. Feldmann (German Patent, 31,237) proposes to add the necessary quantity of lime to gas-liquor, and then filter in a filter-press from the lime mud, and to drive off the ammonia thus set free in a Feldmann still (p. 43).

In Grüneberg's apparatus for the manufacture of

caustic ammonia, the gas-liquor is treated just as in the case of the manufacture of ammonium sulphate, and the resulting gases, which contain ammonium carbonate, sulphide, and aqueous vapour, &c., passed through large lime-washers, and thence into the saturators. Two lime-washers must always be ready, and are used alternately. As soon as the lime in one becomes useless, steam is turned on, and the ammonia it has absorbed driven back into the column and the washer emptied, and refilled with fresh milk of lime.

If the column of the still is properly built, i.e. if the overflow tubes are wide enough, and the perforated caps so fixed that the steam boils through each chamber thoroughly, the whole of the necessary lime may be added at the commencement of the operation without any danger of interfering with the process. The filtration of the gas-liquor as in Feldmann's process, or the large lime-washers used by Grüneberg can thus be avoided.

(*b.*) *Analysis and Application.*—Commercial liquor ammoniæ must be clear and colourless, and quite free from sulphuretted hydrogen and carbonic acid. Its strength is estimated by its specific gravity.

The strongest commercial product, such as is employed for ice and freezing machines, and known as "liquor ammoniæ fortior," has at 15° C. (60° F.), a sp. gr. of 0·885, and contains 35 per cent. of ammonia. The ordinary liquor ammoniæ has a specific gravity of 0·91, and contains 25 per cent. of ammonia. A solution of sp. gr. 0·96, containing 10 per cent. is known in the Pharmacopœia as "liquor ammoniæ caustici officinalis."

The caustic-ammonia prepared from gas-liquor has frequently the great fault that, on long-continued standing it assumes a yellow, or even a brown colour. This coloration is caused by the presence of certain tarry basic impurities, which gradually undergo decomposition. They can only be removed by a second distillation, preferably with the addition of an oxidizing agent.

As one of the strongest basic liquids, liquor ammoniæ is largely used in the arts. An ammonia solution containing 17 per cent. NH_3, is equivalent to a 31 per cent. solution of caustic soda, and it has the further advantage that any excess can be driven off and recovered by distillation, and that the ammonia can be recovered from all waste liquors by boiling with lime. It is chiefly employed in dyeing, calico-printing, bleaching, and in the colour manufacture, and also to a smaller extent in medicine, and for household purposes. The strongest solution is used in ice-machines.

It is transported in tinned iron drums, or in glass carboys. The latter are only used for small quantities and short distances. For calculation of the percentage of ammonia from the specific gravity, see table in Appendix.

4. Concentrated Gas-liquor.

This name has been given to a product containing a larger percentage of ammonia than gas-liqour, and which is obtained from the latter by distillation.

For its preparation, gas-liquor is distilled in one of the continuous stills previously described. The process may be conducted either in the manner

employed for ammonium sulphate, first expelling the volatile salts, and then by addition of lime, the non-volatile compounds, or, as in the liquor ammoniæ manufacture, by adding lime first and then distilling.

In the first case, an ammonia-liquor is produced containing 10—15 per cent. ammonia, of which by far the greater part is in the form of sulphide and carbonate. More concentrated solutions cannot be obtained in this manner, as with vapours containing more ammonia, the pipes frequently become blocked by a deposit of ammonium carbonate. In the second case, a product containing 20—25 per cent. ammonia can be obtained, and in this case the ammonia is chiefly present in the free state, mixed, however, with small quantities of ammonium sulphide and other impurities.

In the manufacture of concentrated gas-liquor by the first named process, the most suitable apparatus is that of Grüneberg or Feldmann (pp. 43, 45), in which, however, the saturator is replaced by an ordinary iron condenser. The amount of lime required is exactly the same as in the manufacture of ammonium sulphate. In the second process, by which in reality a crude caustic-ammonia is obtained, it is preferable to employ the apparatus shown in Fig. 7, the gases being here likewise passed through a simple condenser. The lime required in this case is the same as for the preparation of liquor ammoniæ.

Concentrated gas-liquor is a yellowish liquid, which smells of both ammonia and ammonium sulphide. It is chiefly employed in the manufacture of soda by the ammonia-soda process. The crude caustic

ammonia obtained by the second method is frequently used in chemical works for the preparation of ammonium salts and other products.

The manufacture of concentrated gas-liquor will probably become of greater importance in the future, as it is the best starting-point for the manufacture of valuable ammonium salts, such as the chloride, carbonate, nitrate, &c., the direct preparation of which from gas-liquor is a matter of great difficulty. It may be especially recommended for gas-works, as the process is extremely simple, requires no addition of foreign chemicals, and does not necessarily require to be carried out on a very large scale.

The valuation of either of the products is performed in the usual way. A known weight of the liquor (about 10 grms.) is diluted to 500 cc.; 50 cc. of the solution are distilled with caustic soda, and the vapours evolved passed into 15 cc. of normal acid. Supposing that on titration 3 cc. of acid are found to have remained unsaturated, then 12 cc. of acid have been neutralized. As 50 cc. of solution correspond to 1 grm. of original liquid (assuming that exactly 10 grms. have been taken) it contains $100 \times 0{\cdot}017 \times 12 = 20{\cdot}4$ per cent. of ammonia.

For its transport either tanks on trucks, or iron barrels are employed.

5. Sal-Ammoniac.

(*Ammonium Chloride, Chloride of Ammonia, Ammonii Chloridum.*)

(*a.*) *Manufacture of crystallized Sal-ammoniac.*—

The manufacture of sal-ammoniac is very old. As has already been mentioned, it was obtained in the middle ages from camel's excrement, and came into Europe under the name "sal-ammoniacum." Until the middle of last century, the whole of the European supply came from Egypt, but at the present time it is obtained exclusively from gas-liquor.

The apparatus employed for the manufacture of ammonium sulphate can also be used for preparing sal-ammoniac, with the single exception that the saturator must be closed and constructed of stone. Lead is easily attacked by hot hydrochloric acid, and must therefore be avoided as far as possible in the construction of the apparatus. The saturator is filled with acid of sp. gr. 1·1,* and ammonia passed in until it is completely saturated. The solution formed contains about 25 per cent. of sal-ammoniac, and is pumped into an evaporator, the saturator being then refilled with acid.

The evaporator consists of a wooden vessel, about 39 feet long, 6 feet broad, and 18 inches deep, lined internally with lead. Through it passes a coil of stout lead pipe, 20—26 yards in length which is connected with the steam supply. At the end of the coil a vessel is placed, so arranged as to catch the water which condenses in the pipe, without allowing the steam to escape. As soon as the solution has so far evaporated that a film of salt separates on the surface, it is run by means of a siphon into a leaden vessel, and allowed to crystallize. The salt which separates is fished out

* Strenger acid must never be employed, as it then loses hydrochloric acid gas when hot.

by wooden shovels, and spread out on drying-boards, the latter being so placed that the drainings run back into the crystallizing vessel. The mother-liquor is then pumped back into the evaporator, and after filling up with fresh sal-ammoniac solution, again evaporated.

Especial care must be taken that the sal-ammoniac solution never comes in contact with iron, for, as already stated, the solution decomposes slightly on heating, a little ammonia being evolved. The hydrochloric acid thus set free remains behind, and on this account the hot solution has always an acid reaction and attacks iron. Sal-ammoniac containing iron may be obtained white by crystallization, but the crystals become yellow or red on standing in the air.

(*b.*) *Other methods of preparation* of sal-ammoniac are largely employed in chemical works in which certain metallic chlorides are obtained as bye-products. Thus, for example, gas-liquor is often worked up with calcium, magnesium, and even manganese chloride for the preparation of sal-ammoniac. The gas-liquor contains its ammonia chiefly in the form of carbonate, and therefore on addition of the solutions of any of these chlorides, the carbonate is decomposed with formation of sal-ammoniac, and precipitation of the insoluble metallic carbonate. These are separated by filtration, and the filtrate evaporated to the point of crystallization.

Occasionally hydrochloric acid is added directly to gas-liquor till the solution is slightly acid. The

very dilute solution thus obtained must be separated from the precipitated sulphur by filtration or by settling. The salt obtained is coloured yellow or red, and has a peculiar unpleasant smell. This rough process is still employed in England, in spite of the fact that the price of the "red" chloride is 15—20 per cent. less than that of the white crystalline salt.

A salt which answers all the commercial requirements can be obtained by saturating the so-called concentrated gas-liquor or crude caustic-ammonia with hydrochloric acid. This method has been successfully employed in several French and German works. The advantages of the method are easily perceptible when one considers the losses which occur in the preparation of sal-ammoniac by distillation, and especially the fact that the saturators do not long withstand the action of the hot hydrochloric acid. Even though the renewal of such stone saturators is not very costly, the repairs and setting up take considerable time, and cause undesirable interruptions in the process. A plant for the preparation of concentrated gas-liquor or crude caustic ammonia, combined with the apparatus for saturating the distillate with hydrochloric acid, is not very costly and seems capable of a wide application. With such a plant a manufacturer is in a position to manufacture at will more or less of the various ammonium salts, according to the state of the market.

It seems also probable that sal-ammoniac might be recovered in the ammonia-soda process. This consists, as is well known, in passing carbonic acid

through an ammoniacal solution of common salt, when sodium bicarbonate separates out, and ammonium chloride is also formed.

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$$

Proposals in this direction have been made by Gerlach and others, but it does not seem to have been practically carried out up to the present.

(*c.*) *Sublimation of Sal-Ammoniac.*—Sublimed sal-ammoniac is frequently required in commerce, in place of the crystallized salt; for certain purposes indeed, the crystallized salt cannot be employed at all.

The sublimation is carried out in cast-iron pots, lined internally with fire-brick, which are covered with slightly concave plates, likewise of cast-iron. The crystallized salt used for subliming should be well dried before placing in the pots, which hold about 10 cwt. The sublimation lasts about five days, after which the sal-ammoniac is found on the cover in the form of a solid, fibrous crust about four inches thick, which can be easily detached. This crust is broken up, separated from adhering dirt and impurities, and sent direct into the market.

W. Hempel has found that crystalline sal-ammoniac can be converted into hard stone-like masses without sublimation, by subjecting it at a temperature of 50°—100° C. (120°—212° F.) to great pressure in a hydraulic press. It is to be hoped that practical application of this observation may soon be made. Pressed cakes of sal-ammoniac do occur in commerce, but these are only in a loose

state of aggregation, and break to pieces very easily.

Sal-ammoniac is transported chiefly in barrels, but also frequently in sacks.

(*d.*) *Applications and Valuation.*—The applications of sal-ammoniac are very varied. The sublimed salt is used in soldering, as by its action on the hot surfaces it converts the oxide into chlorides, which latter do not hinder the soldering. The crystalline salt is also employed in the so-called "galvanizing" process, being used in solution for cleansing the articles to be "galvanized" and in the solid form for keeping the surface of the zinc bath unoxidized; it is further employed in dyeing and calico-printing, and for filling certain galvanic batteries. It is used in medicine for catarrh of the stomach and bronchial catarrh.

The chemical examination of sal-ammoniac generally consists in the estimation of ammonia and chlorine, and also frequently of iron, which is detrimental to its employment in dyeing.

The ammonia is best determined by distillation. 10 grm. sal-ammoniac are dissolved in water, diluted to 500 cc., and 50 cc. distilled as usual with caustic soda, passing the vapours into 20 cc. normal acid and titrating back.

The estimation of chlorine is generally made by titration with decinormal silver solution,* using potassium chromate as indicator.

* Decinormal silver solution is obtained by dissolving 17 grms. silver nitrate in 1 litre of water. For the purpose of standardizing it a decinormal solution of common salt (5·85 grms. per litre) may be employed.

5 cc. of the above sal-ammoniac solution are taken, and a few drops of potassium chromate solution added, and the liquid titrated with the silver solution. As soon as the whole of the chlorine is precipitated, the further addition of silver causes a deep red precipitate of silver chromate, thus clearly showing the end of the titration. Suppose 17 cc. silver solution have been used, then, as 5 cc. solution contain 0·1 grms. sal-ammoniac, and 1 cc. decinormal silver solution corresponds to 0·00365 grms. hydrochloric acid, the salt contains $\frac{17 + 0{\cdot}00365 + 100}{0{\cdot}1} = 62{\cdot}05$ hydrochloric acid.

The moisture is determined as in the case of ammonium sulphate ; care must, however, be taken that the temperature does not rise above 100° C. (212° F.), as in that case loss of sal-ammoniac may take place.

The amount of iron present is obtained by treating with a potassium permanganate solution of known strength. The sal-ammoniac solution must previously be treated with a little zinc and hydrochloric acid, to convert all the iron into ferrous salt.

6. Ammonium Carbonate.

(*Sal-volatile, Ammonii Carbonas, Carbonate of Ammonia, Salt of Hartshorn.*)

At the present time ammonium carbonate is prepared by distilling ammonium sulphate with chalk, or directly from gas-liquor.

In its manufacture by the former method an intimate mixture of one part of ammonium sulphate with two parts of chalk is heated in cylindrical iron

vessels, and the vapours evolved led into chambers constructed of stone, where the carbonate is deposited on the walls in crusts. The gases which leave the chamber pass through a small scrubber, where they meet a stream of sulphuric acid, which retains the uncondensed carbonate and free ammonia.

For the distillation horizontal cast-iron cylindrical retorts are employed. These are generally from 7—10 ft. long, and about 18 inches in diameter, and are furnished at both ends with a movable cover. Several of these are heated in one furnace.

When sufficient quantities of the salt have collected in the chamber, the crusts are separated by knocking the walls. The crude salt thus obtained is generally purified by sublimation in pots covered by cylindrical lead caps. To avoid over-heating, the pots are heated in water-baths. The temperature is kept between 70° and 80° C. (158°—176° F.). For every 100 lbs. of ammonium sulphate 76 lbs. of chalk are required. From this mixture a sublimate of 59—60 lbs. of ammonium carbonate is obtained; 6·4 lbs. of free ammonia (corresponding to 25·6 lbs. of ammonium sulphate) are retained in the scrubber, whilst 105 lbs. of gypsum remain in the residue.

From this it is apparent that only three-quarters of the ammonia in the sulphate is obtained as carbonate, the remainder being again converted into sulphate. In order to convert the free ammonia into carbonate, Kunheim (Berlin) passed carbonic acid into the condensation-chambers with very good results. This firm has, however, given up preparing

the carbonate from ammonium sulphate and lime, and now obtains it from pure ammonia gas and carbonic acid. The former is prepared in the same manner as for the manufacture of caustic ammonia, and is passed along with the requisite quantity of carbonic acid into the condensation-chambers, where combination takes place, and the salt is deposited as before.

If the carbonic acid has to be specially manufactured by the action of sulphuric acid on chalk, this process is by no means cheaper than the distillation of the sulphate with lime. Matters are, however, very different where carbonic acid can be obtained cheaply, whether in the form of natural gas, as a product of combustion, from lime-kilns, or as a bye-product from any other manufacture.

Ammonium carbonate is also obtained on the large scale in England from pure ammonia and carbonic acid. The salt thus obtained has, however, not the ordinary composition, but is really *acid ammonium carbonate* $CO\begin{cases} OH \\ ONH_4 \end{cases}$. Whereas the ordinary ammonium carbonate, which is a mixture of ammonium carbamate and acid ammonium carbonate, contains about 31 per cent. of ammonia, the acid salt only contains 21—23 per cent. On exposure to the air it decomposes much more slowly than the ordinary salt, and is generally speaking more stable, and may therefore be especially recommended for household purposes. Unfortunately, it has not so far proved very acceptable, for it smells much less strongly of ammonia than the ordinary salt, and loses

all odour on standing for a short time in the air, and is therefore characterized by the general public as "bad" or "weak." The prices of the acid salt are, of course, much lower, and it is therefore probable that its use will, in spite of the above facts, gradually increase.

Pure ammonium carbonate forms a snow-white crystalline mass; it should dissolve completely in water, forming a colourless solution, and when heated on platinum foil should volatilize without leaving any residue.

For its valuation, the percentage of ammonia is determined by the distillation method, 10 grms. of a good average sample being dissolved in water, diluted to 500 cc., and 50 cc. of this solution distilled with caustic soda. The vapours are passed into 20 cc. of normal acid, the excess of acid determined by titration, and the quantity of ammonia calculated from these data in the usual manner. The ammonia may also be estimated by dissolving the salt directly in normal acid and titrating back with normal alkali.

Ammonium carbonate is employed in medicine, for household purposes, and for baking powder, and also in dyeing and for washing wool and silk.

7. Ammonium Nitrate.

(*Ammonii Nitras, Nitrate of Ammonia.*)

Ammonium nitrate is formed by the double decomposition of Chili saltpetre and ammonium sulphate. On account of its great solubility in water

it would be extremely difficult to obtain by this method a salt free from soda, and it is doubtful whether any technical application of this process has been made.

Its preparation from ammonia and nitric acid is, however, carried out on the large scale. For this purpose it is best to employ crude caustic-ammonia and the ordinary commercial nitric acid. The vessels used as saturators are constructed of earthenware, and are provided with a flue for waste gases, a pipe for passing in the ammonia solution, and a second pipe for drawing off the saturated liquid. A weighed or measured quantity of nitric acid of known strength is placed in the saturator, and the calculated quantity of ammonia solution allowed to pass in slowly from a simple measuring apparatus, until the liquid in the saturator is slightly alkaline. This solution is then evaporated to the point of crystallization. As the salt is hygroscopic and must not remain long in the air, the mother-liquor is separated by centrifugal drainers, and the salt at once packed air-tight.

For analysis 10 grms. are dissolved in 500 cc. of water, and the ammonia determination made in the usual manner by the distillation method. To determine the nitric acid, the residue remaining after distillation is diluted with water, some zinc dust added, and the whole again slowly distilled, the vapours evolved being passed into 50 cc. normal acid. By this means the nitric acid is reduced and given off as ammonia, the amount of which is determined in the ordinary way.

The commercial salt frequently also contains con-

siderable quantities of nitrite, the amount of which may be easily ascertained by titration with potassium permanganate solution.

The demand for ammonium nitrate has increased of late, on account of its employment in the manufacture of explosives. Whether this is likely to last or to increase remains yet to be seen. It is also employed in considerable quantity for the preparation of nitrous oxide (laughing-gas). This gas, which is so largely used by dentists, comes into commerce now in the liquid state, being kept in strong iron bottles. According to Professor Hofmann, almost the whole of the liquid nitrous oxide is supplied to dentists by two firms, viz. Barth and Co., London, and Losse, Berlin. The wrought-iron bottles hold, as a rule, about two pounds of liquid, which corresponds to about 100 gallons of gas. Such a flask is sufficient for 50—60 operations.

8. Ammonium Thiocyanate, or Sulphocyanide.

This salt, which occurs in small quantity in gas-liquor, has of late acquired considerable importance.

Its mode of formation from carbon bisulphide and ammonia or ammonium sulphide has already been described (p. 17). Up to the present this method has not been employed on the large scale, although several proposals in this direction have been made. Thus, J. Schulz proposes the following method:—600 parts of 95 per cent. alcohol are mixed with 800 parts of caustic ammonia of sp. gr. 0·91, and then to these 350 parts of carbon bisulphide added, the

alcohol distilled off, and the solution evaporated to the point of crystallization. The yield of dry sulphocyanide is 280 parts.

On the manufacturing scale, it is chiefly obtained from spent-oxide, by a method which is described later on (p. 98).

The recovery of ammonium sulphocyanide or other sulphocyanides from gas-liquor is not largely practised. Experiments on the large scale in this direction have been undertaken in several works, but no important results have been published. R. Gasch has attempted to arouse ammonia manufacturers to pay more attention to this point, for he states that there is no great future before its manufacture from spent-oxide, as the amount which the latter contains is due to faulty condensation, and therefore the more the condensing apparatus is improved, the less will be the quantity obtainable from this source.

By proper working 2·4 lbs. of sulphocyanide can be obtained from every 100 gallons of gas-liquor. In his proposals Gasch appears to favour the process of precipitation by copper vitriol. If any process for the recovery of this compound from gas-liquor has any future before it, this must take the form of precipitation; for when the small quantity it contains is considered, no other method appears practicable.

The addition of a solution of copper vitriol containing sulphurous acid to one of a sulphocyanide at once precipitates copper sulphocyanide as a fine, white, quickly-settling powder. This precipitate can be easily separated on the large scale by filter presses. If the copper sulphocyanide be then treated

with ammonium sulphide, copper sulphide is precipitated, and ammonium sulphocyanide formed. The latter is obtained pure on filtration and evaporation, whilst the former is reconverted into copper vitriol by roasting, and this used for precipitating a fresh quantity of gas-liquor. Ammonium sulphide may be replaced by other soluble sulphides or oxides, and thus the different salts obtained, just as in the manufacture of these salts from spent-oxide (p. 100).

The quantity of sulphocyanides in the different gas-liquors varies considerably, the richest being the English liquors. Apart from differences in the coal employed, the method of working and condensing apparatus also considerably affect the amount.

Ammonium sulphocyanide, as well as the other sulphocyanides, is employed in dyeing and calico-printing in increasing quantities. A yellow colouring matter termed "Canarine" has also been obtained from it, but this seems at present to have no great practical value. The use of these salts in the manufacture of explosives, which has recently been proposed, has probably no great future, on account of their hygroscopic nature.

9. Ammonium Phosphate.

(*a.*) *Proposals for its Manufacture.*—Up to the present time the practical application of this salt has been very limited. Its manufacture has been attempted at Heilbronn gas-works by Raupp.

The phosphoric acid there employed was a thick,

milky liquid, containing 50 per cent. P_2O_5, of which, however, only one-half was present in the form of free acid, the remainder being combined with lime. 655 lbs. of this acid were placed in a wooden tub, and the ammonia given off by 500 gallons of gas-liquor passed in. At first the liquid frothed up considerably, but after a time the evolution of gas ceased, and a dark, greyish-green thin liquid was formed, which gradually became white, and finally assumed the appearance of lard. This was dried in shallow lead pans, and thus obtained as a greyish-white, extremely hard mass, which required grinding before it could be employed as manure. The yield of the salt, which contained 9·6 per cent. nitrogen and 42·9 per cent. phosphoric acid, was 565 lbs. At first, no purchasers for the product could be found, but finally the Agricultural Institute took it at a price corresponding to the ordinary prices of nitrogen in form of ammonia, and of phosphoric acid. The experiments made to determine its value as a manure had very good results.

Unfortunately the price of the salt is extremely high. The fact that it absorbs moisture from the air and balls together is a further hindrance to its employment. It is manifest from these facts, and from the above-mentioned difficulties of preparation, that it is useless to manufacture this salt.

(*b.*) *Ammonium Superphosphate.*—With ammonium superphosphate matters are quite different. According to Bolton and Wanklyn's process, the ammonia in coal-gas is separated by passing it over superphosphate placed in the ordinary oxide of iron purifiers. The process was first tried in the Munich

gas-works, and has been introduced in many other places during the last few years.

By this process the ammonia is not only absorbed quickly, but also almost completely. One condition must, however, be fulfilled, viz. that the gas is free from tarry matters, as the latter speedily destroy the absorptive power of the superphosphate. In the Munich gas-works it was found that, whereas by the ordinary process of washing with scrubbers, 260 grains of ammonia per 1000 cubic feet remained in the gas only 10 grains could be found after the purification with superphosphate. This can absorb up to 7·5 per cent. of ammonia, and contains then also 0·46 per cent. sulphocyanide. The fears which were at first expressed that the presence of the latter would be deleterious to the growth of plants have not been verified in the experiments made by the first authorities.

The advantages of the process are that it causes a more complete separation of the ammonia than the scrubbers, and that a better price can be obtained for the ammonium superphosphate than for the gas-liquor. It seems therefore probable that the process has good prospects before it, for though it will probably never replace the scrubbers in large gas-works, it is invaluable as a subsidiary method of purification.

10. Ammonium Chromate.

Ammonium bichromate was formerly manufactured

on the large scale more frequently than at present, especially in England.

The chrome-iron-ore is roasted with soda in a furnace, the process corresponding exactly to the first portion of the manufacture of potassium bichromate. The mass thus obtained is lixiviated with water, and sufficient sulphuric acid added to set free the chromic acid. The free acid is then neutralized with concentrated gas-liquor or crude caustic-ammonia, and the liquid thus obtained evaporated till the salt crystallizes out. In the roasting process lime may be substituted for soda.

If hydrochloric acid be employed to set free the chromic acid, then on evaporation of the neutralized liquid common salt separates out, whilst ammonium chromate remains in solution, and may be obtained pure by further evaporation of the liquid. When sulphuric acid is used, it is extremely difficult to separate the chromate from the sulphate also formed.

According to a patent (No. 8602) taken out by J. Park, calcium chromate is treated with the necessary quantity of sulphuric acid to convert it into bichromate, and to this ammonium sulphate is added, the whole filtered, and evaporated to the point of crystallization.

Since the price of potash salts has been so much reduced by the discovery of the Stassfurt deposits, there is no probability that ammonium bichromate will ever seriously compete with the corresponding potassium salt.

Ammonium chromate is employed in calico-printing.

11. Ammonium Oxalate.

For the preparation of the neutral salt a solution of crude oxalic acid is saturated with crude caustic-ammonia, the mixture allowed to settle or filtered through a small filter-press, and the clear solution evaporated to the crystallizing point. The salt thus obtained must be recrystallized from water, the solution being first purified by animal charcoal.

From the solution of this salt the acid salt is readily obtained by the addition of the calculated quantity of oxalic acid. It may also be prepared by neutralizing a weighed quantity of the acid with crude caustic-ammonia, and then adding the same quantity of oxalic acid, filtering and evaporating.

Ammonium oxalate is used in analysis, medicine, photography, and calico-printing.

12. Ammonium Sulphide.

The ammonium sulphide occurring in commerce is not prepared on the manufacturing scale. For its preparation sulphuretted hydrogen is passed into caustic ammonia until it is no longer absorbed. The solution should give no precipitate with a solution of magnesium sulphate, otherwise free ammonia is still present.

Beyond its use in analytical chemistry ammonium sulphide has no practical applications. It has been occasionally employed in medicine, and also for etching copper objects.

13. Ammonium Vanadate.

This compound, in which the ammonia plays an unimportant part compared with the vanadic acid both as regards price and application, is only mentioned here for the sake of completeness. The price of the salt is more than 4*l.* 10*s.* per lb.

Vanadic acid occurs in several rare minerals, the most important of which is Mottramite (Pb Cu) $(VO_4)_2$. The Magnesium Metal Company in Patricroft (near Manchester) obtain ammonium vanadate from this on the large scale. The mineral is extracted with hydrochloric acid, and the extract evaporated with an excess of sal-ammoniac, when crude ammonium vanadate separates. This is recrystallized several times, and then ignited, and the residue (V_2O_5) dissolved in ammonia. The solution is filtered and evaporated.

The salt is used in calico-printing and wool-dyeing for the formation of black. One part of ammonium vanadate is sufficient to convert 1000 parts of aniline salt into aniline black, if a sufficient quantity of potassium chlorate is also present.

14. Waste Products from the Gas-liquor.

The waste products formed in the manufacture of the above salts from gas-liquor are three in number: (1) the gases evolved from the saturators; (2) the lime-mud; (3) the waste liquor.

(*a.*) *Waste Gases.*—The two chief constituents of the waste-gases are carbonic acid and sulphuretted

hydrogen, the former being present in the greater quantity; they also contain smaller quantities of cyanogen, sulphocyanic acid, and other organic sulphur compounds, besides being invariably more or less diluted with steam. It is now compulsory to treat these gases in such a manner that they cause no nuisance or damage when they pass into the atmosphere. The plan generally adopted is to pass them into the flues of the nearest convenient boiler, in order to burn them. A complete combustion of the sulphuretted hydrogen to sulphurous acid very rarely takes place on account of the large quantities of steam and carbonic acid present; the gases pass therefore, largely unaltered, into the chimney, and thence into the atmosphere, where they speedily become so diluted as to be innocuous. If, however, no tall chimney is available, it may happen that in cool, damp weather the aqueous vapour condenses quickly and falls to the earth, where it may cause considerable damage and nuisance on account of the sulphuretted hydrogen, &c., that it contains; in that case it is necessary to get rid of the aqueous vapour by a suitable condenser, and then pass the dried gases under the boiler fires, and burn them properly.

The Ammonia-gas Purifying and Alkali Company have patented the following process for recovering sulphur (to the extent of 90 per cent.) from the waste gases (Claus' process). After condensation of the aqueous vapour, the remaining gas is passed, together with the necessary quantity of air, into a specially constructed kiln, where it comes in contact with red-hot lumps of oxide of iron and firebricks. Under these

conditions sulphuretted hydrogen burns to water and sulphur vapour, which are condensed in a series of air-cooled chambers. The necessary amount of air is ascertained by analysis of the gases passing out of the kiln ; if too little air is present, the gases contain sulphuretted hydrogen, if too much, they contain sulphurous acid. The gases should therefore only contain traces of these compounds, along with nitrogen, carbonic acid, and steam. As a general rule a quantity equal to three-quarters of the volume of the waste-gases is sufficient. The chambers remain continuously at work, except during a few short intervals, for about six months, at the end of which time the deposit is removed. The sulphur obtained in this manner is almost chemically pure.

The process is said to yield very good results at Stafford and Belfast.

(*b.*) *The Lime-Mud* is a useless and troublesome waste-product. If allowed to pass away with the waste-liquor, it would speedily block up all drains, and must therefore be separated by filtration or by allowing it to settle. As a general rule the waste-liquor is run into a large pool, and allowed to stand until it becomes clear. The mud is from time to time dug out and carried away.

(*c.*) *The Waste-Liquor* is not less troublesome than the foregoing. It contains calcium chloride, cyanide, sulphide, thiosulphate, sulphate, and hydroxide, tarry acids, &c. It has a brown colour and unpleasant tarry smell, and causes constant complaints from the whole neighbourhood. Even though it does not give off vapours dangerous to health, it

makes any small watercourses practically useless for other commercial purposes. In the case of watercourses contaminated with decayed organic matter it is to a certain extent beneficial, inasmuch as it has a disinfecting action. No fish can of course live in water which is strongly contaminated with it.

At present no suitable method of rendering the waste-liquor innocuous is known. Lunge has, however, recently proposed to cause a precipitate of alumina or oxide of iron in the clarifying pool, by which means the tarry matters and other impurities would also be precipitated.

III.

UTILIZATION OF THE "SPENT-OXIDE."

1. Chemical Changes in the Purification of Coal-Gas by Ferric-Oxide.

(*a.*) *Separation of Sulphur in the Spent-Oxide.*—The gas obtained from the distillation of coal, after being freed from tarry matters and ammonia in the air-condensers and scrubbers, still contains considerable quantities of sulphuretted hydrogen and other sulphur compounds, the removal of which is absolutely necessary. The combustion of gas containing these products in inhabited rooms would speedily so contaminate the atmosphere as to make it unbearable.

In order to purify the gas from these products, it was formerly passed through purifiers containing "Laming's mixture." This was prepared by mixing iron vitriol and slaked lime with sawdust, and allowing the moistened mass to stand for some time in the air before placing in the purifiers. When the mass ceased to work effectively, it was again exposed to the air, frequently moistened and stirred, and then, after a further addition of lime, once more used for purifying the gas. It was believed at that time that the sulphuretted hydrogen was decomposed by the

ferric oxide with formation of sesquisulphide of iron and water.

$$Fe_2O_3\ 3H_2O + 3H_2S = Fe_2S_3 + 6H_2O.$$

Then on exposure to the air it was supposed that this sesquisulphide was oxidized to iron vitriol with separation of sulphur.

$$Fe_2S_3 + 8O = 2\ FeSO_4 + S.$$

The further addition of lime was supposed to reconvert the iron vitriol into hydrated ferrous oxide, which took up oxygen from the air, forming hydrated ferric oxide.

In 1866 it was found from a number of analyses made at the Munich gas-works that the quantity of sulphur which is separated by the revivification of the mass is three times as large as is possible according to the above theory. This unexpected result caused further investigations to be made, and it was found that in Laming's mixture the oxide of iron alone takes part in the reaction. This absorbs sufficient sulphur from the gas to form iron sesquisulphide; and on exposing the saturated mass to the air, this compound is oxidized, ferric oxide being re-formed, and the whole of the sulphur separated out in the free state. The following simple equations explain the reaction:—

$$Fe_2O_3\ H_2O + 3H_2S = Fe_2S_3 + 4H_2O$$
$$Fe_2S_3 + 3O + H_2O = Fe_2O_3\ H_2O + 3S.$$

As soon as this was proved, the use of lime in the purifying mass was dispensed with, and oxide of iron alone employed.

The cheapest form of iron oxide is natural bog-iron ore. This contains 50—70 per cent. of ferric oxide

and is especially suitable on account of its porous nature, as in that condition it offers comparatively little resistance to the passage of the gas. The mixture proposed by Lux, which is an alkaline hydrated oxide of iron, is also highly spoken of. A mass of similar composition to this is also obtained in working up bauxite. The treatment with alkali at high temperatures is said to render the oxide more active, so that it absorbs sulphuretted hydrogen more energetically than any other mixture. Certain industrial bye-products, which consist for the most part of ferric oxide, are also employed in coal-gas purification; among these may be mentioned the spent pyrites from the sulphuric acid manufacture, and the ferric oxide precipitated in the preparation of aniline; care must, however, be taken that these are not too dense. In order to render the mass more porous, the oxide is frequently mixed with sawdust or small coke.

The reactions which take place in the operation are not quite so simple as shown in the above equation; secondary reactions also invariably take place, but these are very small compared with the chief reaction.

Various chemists have found that the ferric-oxide can absorb more sulphur than is accounted for by the theory. Thus, for example, Deike passed sulphuretted hydrogen for 24 hours over 2236 grams of powdered ferric hydroxide, and found that the mass then contained 10 per cent. more sulphur than demanded by theory. Cox and others assume that the sesquisulphide of iron can be to some extent decomposed, even in absence of oxygen, by the action of moisture. The

spent mass taken from the purifier is in fact found to contain not only the sulphide of iron, but also considerable quantities of sulphur, even before exposure to the air. In revivifying the mass in the air, besides the oxidation of iron sulphide to sulphur and ferric oxide, a certain amount is converted into basic ferrous sulphate.

The importance of the separation of the sulphur in the purifiers is shown by the following statement of Knublauch :—

Total weight of coal used per annum . . .	40,000 tons.
Sulphur separated in gas-liquor	16 „
„ „ „ the spent-oxide . . .	114 „

For every ton of Westphalian coal used, 6·3lbs. of sulphur are deposited in the purifiers.

(*b.*) *Separation of Nitrogen Compounds in the Purifiers. Composition of certain Spent-Oxides.*—Besides sulphur, other substances are retained by the oxide in the purifiers. Considerable quantities of cyanogen are absorbed, and remain in the form of ferrocyanides, and ammonium sulphocyanide and sulphate also occur in varying quantities.

Although the processes by which the separation of sulphur takes place are fairly clear, the formation of ferrocyanides and sulphocyanides is at present quite inexplicable. It can hardly be assumed that the ammonium sulphocyanide reaches the purifiers in the form of vapour and is there deposited, for it is not particularly volatile. It is therefore probably more correct to assume that it is formed by reactions taking place in the purifier itself, which require further investigation. It is as yet unknown from what original constituent or constituents of the gas the

ferrocyanides are formed. It is certain that the gas contains no hydrocyanic acid or ammonium cyanide, for on passing the gas through an acidified solution of ferric chloride no trace of Prussian-blue is obtained; only when the free acid is neutralized by the ammonia contained in the crude gas is Prussian-blue precipitated together with iron sulphide.

It should also be noted that the substance occurring in the spent-oxide is not pure Prussian-blue, but an insoluble compound of the latter with ammonia. The ammonia contained in the mass cannot be completely extracted with water; a certain amount always remains behind, and must be set free by alkali. Moreover, sulphocyanides occur both in soluble and insoluble form. It is well known that Prussian-blue, when obtained by precipitation, frequently carries down with it other salts from which it cannot be separated by washing, and it is not improbable that in the spent-oxide it unites with a portion of the sulphocyanide in a similar manner.

According to Knublauch the composition of the spent-oxide depends not merely on the condition of the original mass, but also to a large degree on the purification in the wet way, i.e. the removal of ammonia in the condensers and scrubbers. If this is faulty, the ferrocyanides are only formed in small quantity. In the gas-works at Cologne, where the wet purification is in very good order, the spent-oxide contains as much as 25 per cent. of Prussian-blue, an amount which is probably equalled at no other works.

It is interesting to note the relative quantities

of nitrogen obtained as ammonia and as cyanogen in the dry distillation of coal.

According to W. Foster :—

0·251% of the coal = 14·51% of the nitrogen form ammonia.
0 027 „ „ „ = 1·56 „ „ „ „ cyanogen
0·610 „ „ „ = 35·26 „ „ „ remain in the gas
0·842 „ „ „ = 48·67 „ „ „ „ „ coke

According to Knublauch :—

31—36% of the nitrogen remain in the coke.
10—14 „ „ „ form ammonia.
1·5—2 „ „ „ „ cyanogen.
1—1·3 „ „ „ remain in the tar.

The following table shows the quantity of sulphur, Prussian-blue, ammonium sulphocyanide, and the total ammonia, contained in various dried spent-oxides :—

	Per cent. of sulphur.	Per cent. of Prussian-blue.	Per cent. of ammonium sulphocyanide.	Per cent. of total ammonia.
1	31·0	6·0	trace	1·1
2	42·1	5·2	2·8	0·8
3	40·5	4·1	0·5	1·5
4	37·3	6·4	0·4	0·7
5	36·4	4·0	0·5	1·0
6	50·6	4·5	2·0	0·4
7	25·1	3·3	trace	0·9
8	38·8	2·1	3·7	1·2

Bunte gives the following analysis of a spent-oxide which had been used eight times :—

0·77% ammonium sulphate.
4·40 „ „ ferrocyanide and cyanide.
14·08 „ „ sulphocyanide.
16·82 „ hydrated iron oxide.
11·12 „ Prussian-blue.
33·50 „ sulphur.
19·31 „ saw-dust, tar, &c.

A. Wagner found in a frequently used spent-oxide :—

21·7 % iron oxide,
45·5 „ sulphur,
4·35 „ ammonium sulphocyanide,
trace of Prussian-blue.

From these examples the varying composition of the spent-oxide is very manifest.

(*c.*) *Revivifying the Spent-Oxide.*—This is of especial importance, not merely for the gas purification, but also for the subsequent processes in working up the spent-oxide; for the amount of valuable substances formed in the latter depends largely upon the number of times it has been used and revivified. The general method of revivifying consists in shovelling the mass out of the purifiers on to special floors, where it is frequently turned over and moistened. Here and there this process has been replaced by revivification in the purifiers themselves. For this purpose the used-up purifiers are disconnected, and a stream of air forced through them for several hours by means of a steam ejector or other draught. The purifiers can then be immediately put into action again. The cover of the purifier must, however, be occasionally removed in order to stir up the mass, which becomes caked together from the separation of sulphur. It is manifest that this process is very much simpler and more convenient than the first named.

A process which promises to become of the greatest importance is the *continuous* revivification of the spent-oxide "in situ." For this purpose oxygen is mixed with the crude gas before it reaches the purifiers, in sufficient quantity to oxidize to ferric oxide all the sulphide of iron formed by the sulphur compounds in

the gas. The mass can then be allowed to remain in the purifiers and in the gas, until the quantity of sulphur deposited causes considerable diminution in the absorptive power of the mass. To judge from experiments made on the large scale in certain English gas works, the process promises to be successful. 2·5 cubic feet of oxygen* for every 1000 cubic feet of gas were found to be sufficient; the spent oxide formed contained 50—60 per cent. of sulphur, and the illuminating power of the gas was in no way diminished.

2. Treatment of the Spent-Oxide.

(*a.*) *The Raw Material.*—The different varieties of spent-oxide show not only great chemical but also great physical differences. From the larger works the mass is, as a rule, free from all those mechanical impurities, such as saw dust and small coke, which are frequently added in smaller gas works, to render the mass more porous. Now and again varieties are found which contain large quantities of lime, for which many gas-engineers have still unfortunately a great preference. Fresh varieties, which have not lain long in the gas-works, frequently contain naphthalene, and possess its characteristic penetrating smell; other kinds are quite odourless, having lost their volatile tarry constituents by lying for a long time in the open air, and these have also too frequently had a portion of their soluble salts washed away by the rain. This dissimilarity in the spent-oxides is a great source of inconvenience to those engaged in its treatment.

* Brin's oxygen, which can now be cheaply obtained, was employed.

It is to be hoped that in the course of time all gas works will find it to their advantage to prepare it in as homogeneous a form as possible. The mechanical impurities, which frequently amount to 50 per cent. of the whole, should especially be got rid of, as they not only lower its value, but often cause great additional difficulty in the recovery of the various products.

A preliminary treatment of the spent-oxide is only necessary when the ferrocyanides are to be recovered. In this case the oxide must be powdered, as it contains lumps from $\frac{1}{4}$ to 1 inch in diameter, which are held together by the deposited sulphur, and are not penetrated by the agents employed. It is quite sufficient to pass the damp mass between grooved cast-steel rollers.

For the extraction of sulphur the mass must be quite dry. To this end it is allowed to lie under cover in the air for considerable time, under which conditions not only the moisture, but also the naphthalene and tarry impurities are given off.

The Analysis of Spent-Oxide is of great importance; as by this alone is it possible to ascertain its value, and to determine the method by which it shall be treated.

Estimation of Moisture.—A weighed quantity of a good average sample is dried in a dessicator over calcium chloride.

Estimation of Sulphur.—This is estimated as raw sulphur by extraction with carbon bisulphide. Any glass extracting apparatus may be employed which is sufficiently large to extract about 100 grms. From a good average sample 50—100 grms. are taken and extracted with carbon bisulphide, until the

liquid passing off is no longer coloured. After evaporating off the solvent the residual sulphur is melted and weighed.

Estimation of Sulphocyanides.—50 grms. of the spent oxide, after freeing from sulphur, are extracted with warm water, and the solution partially evaporated on the water-bath, acidified with sulphurous acid, and precipitated with an excess of copper sulphate solution. The white precipitate is collected on a weighed filter, dried, and weighed. 121.5 grms. of copper salt correspond to 76 grms. of ammonium sulphocyanide. If no chloride, cyanide, or ferrocyanide is present, this estimation may be very quickly made with decinormal silver solution. 10 cc. of this are taken and mixed with a few drops of nitric acid and ferrous ammonium sulphate solution, and titrated with the solution of sulphocyanide diluted to a known volume, till a red coloration is produced. Suppose that the aqueous extract of 50 grms. spent-oxide has been diluted to 500 cc., and that 20 cc. of this solution are required for the titration of 10 cc. decinormal silver solution; then the whole liquid contains $\frac{10 \times 0{\cdot}0076 \times 500}{20} = 1{\cdot}9$ grms., and the spent-oxide contains $2 \times 1{\cdot}9 = 3{\cdot}8$ per cent. of ammonium sulphocyanide.

Estimation of Ferrocyanides.—The residue from the extraction of the sulphocyanide, corresponding to 50 grms. spent-oxide, is warmed for some time with an excess of caustic soda. Too large an excess should be avoided, and the whole well stirred. The mixture is then filtered, the residue washed with hot water, and the filtrate boiled with pure ammo-

nium chloride or sulphate solution until no further smell of ammonia is perceptible. In this manner the alumina dissolved by the caustic soda is precipitated. Its elimination is necessary, as it is precipitated together with Prussian-blue even in slightly acid solutions; moreover, by its precipitation dark tarry matters are likewise carried down, and the solution thus becomes clearer. After filtering off the alumina, the solution is slightly acidified with hydrochloric acid, heated to boiling and poured into a hot dilute solution of ferric chloride. The Prussian-blue precipitated is allowed to settle, the dark red liquid poured off, and the precipitate well washed by decantation. It is then brought on to a filter and washed with hot water till the filtrate is free from iron, dried, and ignited in a platinum crucible to which the air has access. It is thus converted into ferric oxide, which is weighed, and the quantity of ferrocyanide calculated from the weight found. 560 parts of ferric oxide correspond to 636 parts ferrocyanogen ($Fe(CN)_6$) and to 860 parts of Prussian-blue.

The composition of Prussian-blue varies according to the conditions under which it is precipitated. If iron be not present in excess, a compound of Prussian-blue with potassium or sodium ferrocyanide separates. Moreover, under certain conditions, the precipitate contains also potassium or sodium sulphate. It is therefore necessary to adhere exactly to the method of precipitation given above.

In many cases a volumetric method, which the author has employed for a long while, is quite sufficient. 42·2 grms. of pure dry potassium ferro-

cyanide ($K_4Fe(CN)_6 + 3H_2O = 422$) are dissolved in water and diluted to a litre. A dilute, slightly acid ferric chloride solution is placed in a burette, and 10 cc. of the ferrocyanide solution titrated with it. So long as an excess of ferrocyanide remains in solution, no Prussian-blue is precipitated. If a drop of the dark blue liquid be placed on filter paper, it spreads out to a uniform blue spot. As soon, however, as all ferrocyanide is converted into Prussian-blue, the spots do not spread uniformly, but give a blue patch in which the particles of precipitated Prussian-blue are easily seen. The end of the titration may be accurately detected by employing filter paper previously soaked in ammonium sulphocyanide solution. The slightest excess of iron is then recognized by the fact that the blue particles no longer appear on a white, but on a yellow or red ground. The strength of the iron solution having thus been ascertained, it is diluted to correspond with the ferrocyanide solution, and again compared with the latter in the manner above described. With this iron solution, all liquids containing ferrocyanides can be titrated with fairly accurate results. The liquids must, however, be neutral and free from alumina. Let us suppose that 20 cc. of the neutralized caustic soda extract (diluted previously to 500 cc.) require 30 cc. of ferric chloride solution, then as 1000 cc. ferric chloride solution correspond to 21·2 ferrocyanogen ($Fe(CN)_6$) the whole extract contains $\frac{\frac{21\cdot2 \times 10}{100} \times 500}{20} = 5\cdot3$ grms. $= 2 \times 5\cdot3 = 10\cdot6$ per cent. of ferrocyanogen.

Estimation of Ammonia.—This estimation is best

performed by the azotometric method (p. 25). For the *total ammonia* 3—4 grms. of the spent-oxide are weighed out and placed in the inner cylinder of the apparatus, and the analysis performed in the usual manner. To determine the quantity of soluble ammonia, 50 grms. of spent-oxide are extracted with water, the extract diluted to 200 or 250 cc., and 10 cc. analyzed by the azotometer.

(*b.*) *Recovery of Sulphocyanides.*—The recovery of sulphocyanides from spent-oxide forms at the present time a small but flourishing industry, the process being carried out by about ten different firms.

Until recent years, the spent-oxide was used exclusively for sulphuric acid manufacture. It was roasted in the ordinary kilns, thus converted into sulphurous acid, and this oxidized to sulphuric acid by the usual process. The residue was then again employed for gas purification. The increase in the demand for sulphocyanides, due to their employment in dyeing and calico-printing, caused manufacturers to turn their attention to the recovery of the ammonium salt from the spent-oxide, the first attempts being made in England. The process, which has in the meantime been improved and extended to the recovery of other sulphocyanides, is still being successfully worked.

Only such varieties of spent-oxide as are fairly rich in sulphocyanides are worked up. They are directly extracted with water, in an apparatus constructed in a similar manner to that used for the lixiviation of black-ash, and known as Buff and Dunlop's or Shank's appara-

tus. It consists of a number of wooden tanks arranged in a series, and so connected that the tank containing the fresh spent-oxide is extracted with a liquor which has already passed through several other tanks. After treatment with the fresh spent-oxide, this liquor is pumped off and evaporated. The oxide is next washed with a more dilute liquor from another tank, and the liquor thus obtained pumped into a vessel containing fresh spent-oxide, and then evaporated. The first quantity of spent-oxide is then washed for the third, fourth, and fifth time with liquors which are each time more dilute, and finally with pure water, the liquors formed being in each case conveyed into tanks containing richer spent-oxide. The thoroughly extracted mass is then removed from the tank, and the latter re-filled with fresh spent-oxide.

The liquor thus obtained is by no means very concentrated, and rarely contains more than 2 per cent. of ammonium sulphocyanide. The strength, of course, depends largely upon the amount originally contained in the spent-oxide. Besides ammonium sulphocyanide, the liquor always contains more or less ammonium sulphate, gypsum, and ferrous sulphate. If the liquor is sufficiently pure, it is directly evaporated, and the ammonium sulphate allowed to crystallize out, and then the mother-liquor further evaporated until the ammonium sulphocyanide also separates. In many cases, however, this method of treatment would yield very unsatisfactory results. The method of precipitation with copper vitriol already described (p. 76) might then be employed. Unfortunately, this method is somewhat indirect, and requires a large plant,

on which account it can scarcely be employed, except in large works. A simpler method is the following :— The liquors are so far evaporated that the gypsum and the greater portion of the ammonium sulphate separate out, and the mother-liquor then boiled with baryta in a boiler lined with lead, the requisite quantity of baryta being previously ascertained by analysis of the liquor. Steam is now blown through the liquor, until no more ammonia is given off. (The ammonia gas thus set free may be used for the preparation of caustic ammonia). The solution of barium sulphocyanide formed in this manner should still contain a slight excess of baryta, which is removed by passing carbonic acid through the liquid until it has a neutral reaction. The milky liquid is then filtered from the precipitated barium carbonate, sulphate, and ferrous hydroxide by means of a filter-press. The filtrate has frequently a deep yellow or brown colour, which may be to a large extent removed by the addition of animal charcoal and re-filtration. The filtered and decolorized liquid is then evaporated in a wooden vessel lined with lead, and heated by means of a steam-coil. The evaporation is continued until large bubbles form on the surface, which are covered with a film of salt. The contents of the evaporator are then run into a wooden barrel, likewise lined with lead, and provided with a tight-fitting cover. In the bottom of the barrel is an opening, which can be closed by a wooden plug. When the liquid is quite cold, the plug is knocked out, the mother-liquor allowed to run off, and the salt at once thrown on to centrifugal drainers, and quickly packed air-tight.

The product obtained in this way crystallizes in beautiful needles, and though generally slightly yellow, is almost pure. Barium sulphocyanide is preferred to the other salts for dyeing purposes, and therefore obtains a higher price.

The spent-oxide after the extraction of the sulphocyanides, is employed for the sulphuric acid manufacture in the usual manner, unless the sulphur has been previously extracted according to the method described later on, in which case the ferrocyanide can also be recovered.

(*c.*) *Recovery of Ferrocyanides.*—The recovery of ferrocyanides from spent-oxide is not yet carried on to any great extent. The chief information on the point is found in the German Patent records.

The most important process is that of Kunheim and Zimmermann. (German Patent, No. 26,884). The spent-oxide is first freed from sulphur by treatment with carbon bisulphide or light petroleum-ether, and afterwards extracted with water to remove sulphocyanides. The mass, after being allowed to dry in the air, is intimately mixed with powdered lime, and heated in a closed vessel to a temperature of 40°—100° C. (104°—212° F.), in order to drive off all ammonia present in the form of insoluble compounds. The resulting mass is then systematically extracted. The calcium ferrocyanide solution, which still contains ammonia, is neutralized and boiled, when the difficultly soluble double ferrocyanide of calcium and ammonium $Ca(NH_4)_2 Fe Cy_6$, is precipitated. This salt on boiling with milk of lime yields a pure solution of calcium ferrocyanide, which may be converted into

Prussian-blue by treatment with iron salts. In order to obtain from it potassium ferrocyanide (prussiate of potash), the solution is partially evaporated, and sufficient potassium chloride added to the solution to form the difficultly soluble potassium calcium ferrocyanide. On boiling this with a solution of potassium carbonate, it is converted into potassium ferrocyanide. The corresponding sodium ferrocyanide may be obtained by substituting sodium carbonate (soda) for potassium carbonate (potash).

In Hempel and Sternberg's process (G. P. 33,936), the spent-oxide is first extracted with water, and then treated with three to four times the theoretical quantity of caustic ammonia at the ordinary temperature. The solution of ammonium ferrocyanide obtained is then converted into either Prussian-blue or potassium ferrocyanide.

S. Marasse (G. P. 28,137) utilizes the ferrocyanides by converting them into sulphocyanides. The spent-oxide, from which the soluble ammonium salts have been extracted with water, is heated in closed vessels with an excess of lime to over 100° C. (212° F.). The end products of the reaction are calcium sulphocyanide and iron sulphide, which are separated from one another by filtration.

Wolfrum's process (G. P. 40,215) combines the working up of the spent-oxide and of the gas-liquor, and these again with the purification and washing of coal-gas. The process can therefore only be carried out in a gas-works.

The spent-oxide is first extracted with dilute sulphuric or hydrochloric acid, and the solution, which

contains considerable quantities of iron, mixed with gas-liquor, the free acid being, however, first neutralized by ferric oxide or iron ochre. By the treatment with acid the ammonium sulphocyanide contained in the spent-oxide is eliminated, whilst the double compound of ammonium ferrocyanide and Prussian-blue is converted into ammonium sulphate or chloride and Prussian-blue free from ammonia, which latter remains in the residue. The sulphur in the residue is extracted by means of carbon bisulphide. The precipitate formed on mixing the iron solution with gas-liquor contains about 30 per cent. of sulphur recoverable by carbon bisulphide, and 40 per cent. of ferric oxide, partly as basic ferric sulphate, and partly as Prussian-blue. After the extraction of sulphur, this residue may be mixed with the iron ochre and used for the gas purification. The desulphurized liquor is freed from excess of ammonia by distillation, and then returned to the scrubbers, and the process repeated until the liquor contains sufficient ammonium sulphate and sulphocyanide to pay for their recovery by evaporation. The residue from the spent-oxide after extraction with acid and carbon bisulphide is utilized for the preparation of potassium ferrocyanide.

The only process which is at present used is that of Kunheim and Zimmermann, for although it is somewhat roundabout, it suits the present requirements better than the other. Hempel and Sternberg's process has the advantage of obtaining the ferrocyanide without previous extraction of the sulphur; the decomposition of the Prussian-blue by ammonia is, how-

ever, incomplete, and the yield of ferrocyanides would be very unsatisfactory. Marasse's process has no great prospects, for the sulphocyanide market would soon be overstocked if all the ferrocyanide of the spent-oxide could be converted into that substance. Moreover, the further treatment of the calcium sulphocyanide solution would not be easy on account of the calcium sulphide which it must inevitably contain. Wolfrum's process is on a sound basis, but the time has not yet come for the management of the gas-manufacture to pass into the hands of chemists, and for the process to be conducted throughout in such a scientific manner as Wolfrum's process demands.

Prussian-blue can only be extracted from spent-oxide by milk of lime and by caustic soda. Caustic potash can hardly come into consideration on account of its price. The extraction with milk of lime does not give by any means good yields. The desulphurized mass must be boiled with milk of lime until no more ammonia is evolved, as otherwise the double salt of calcium and ammonium is formed, which is difficultly soluble, and therefore not readily extracted. This fact alone makes the milk of lime extraction almost impossible in practice, for the thick liquid must be treated for hours with steam before the ammonia is all driven off. In one case an attempt was made to extract the spent-oxide with the waste-liquor from the gas-liquor distillation, but with no great success.

Caustic soda solution decomposes Prussian-blue quickly and completely, and the sodium ferrocyanide formed can be easily extracted. Unfortunately the

larger quantity of the caustic soda is absorbed by the sulphuric acid in the spent-oxide (chiefly present as basic ferrous sulphate), even when the mass has been previously desulphurized and extracted with water.

Spent-oxide which does not contain at least 10 per cent. of Prussian-blue, does not pay for treatment with caustic soda. For example, a mass containing 3 per cent. of Prussian-blue requires theoretically 1·67 per cent. of caustic soda for its decomposition. It is found, however, that even when the spent-oxide has been carefully extracted with carbon bisulphide and hot water, no less than 5—6 per cent. of caustic soda are required. The quantity of basic sulphate in spent-oxide is fairly constant, whether they contain large or small quantities of Prussian-blue. With spent-oxide containing large quantities of ferrocyanides, the loss of caustic soda is therefore much less in proportion, and only in such cases does the extraction pay. The liquors obtained must always be slightly alkaline, as they contain also large quantities of sodium sulphate, which it would otherwise be a matter of impossibility to separate from the sodium ferrocyanide by crystallization.

Sodium ferrocyanide is now being prepared on the large scale by two German firms.

(*d.*) *Extraction of the Sulphur.*—The weakest point in the process for the recovery of the ferrocyanides lies in the fact that the sulphur must be previously extracted. That this is unavoidably necessary, is very clear from the foregoing pages. Kunheim and Zimmerman's process requires that the sulphur should be absent, and any treatment with caustic soda whilst

the sulphur is still present, is, of course, out of the question. Unfortunately, a grey sulphur contaminated with tarry matters is thus obtained, which has but little value. Matters would be very different if the extraction paid its own way, or, better still, was a source of profit. As the matter stands at present, all profits must be obtained from the ferrocyanides, and this is therefore an additional reason why only spent-oxides rich in ferrocyanides are worth extracting.

To desulphurize the spent-oxide without at the same time decomposing the ferro- and sulphocyanides, is by no means an easy matter. High temperatures must be avoided, on which account the sulphur cannot be driven out by roasting or by superheated steam. The only method which can be employed is that of extracting the sulphur with liquids at temperatures under 100° C. (212° F.). Suitable liquids for the purpose are, light-petroleum ether, benzene, and carbon bisulphide. Light-petroleum ether dissolves about 5 per cent. of sulphur at a medium temperature, and 10—12 per cent. at its boiling point. Benzene {B.P. 80° to 100° C. (186—212° F.)} dissolves at the ordinary temperature 2—3 per cent., at 100° C. (212° F.) 15 per cent. of sulphur, whilst carbon bisulphide takes up 40—50 per cent. at the ordinary temperature, and 180 per cent. at 55° C. (131° F.).

The latter solvent is therefore the one usually employed, and it has the further advantages of being cheap, and easily prepared. Unfortunately very few details can be obtained concerning this extraction of sulphur, as the process is rarely worked on the large scale. It is true that large plants for the extraction of oils and

fats have been built, and are working successfully, but it must be borne in mind that the two processes are essentially different, for whereas in the case of oils and fats we have to deal with bodies which are either liquid or melt below the boiling point of water, we have in sulphur a substance which is still solid at that temperature; moreover, in the first case the oils and fats can be easily freed from the last traces of the solvent by steam, whilst with sulphur the slightest condensation of moisture causes the whole liquid mass to solidify.

Different forms of extractor have been proposed by Wegelin and Hübner, Büttner, and Hirzel. A description of Wegelin and Hübner's apparatus, which is known to work well and economically, is given below.

The extractor *A* (Fig. 9), which is provided with a perforated false bottom, is filled with carefully dried spent-oxide. The solvent (in this case carbon bisulphide) is contained in *R*. After the spent-oxide has been placed in the extractor, the manholes are tightly closed, all taps communicating with the outer air shut, and the carbon bisulphide allowed to flow from *R* into the extractor. The liquid trickles through the spent-oxide, and flows through the three-way cock *L*, directly into the evaporator *C*, which is heated by a steam coil. The carbon bisulphide distils off, and the vapour passes into the condensor *B*, the condensed liquid running into *R*, and from there again to *A* and to *C*. The vessel *R* is in communication with the outer air by means of a tube closed with a valve; through this tube is evolved the air contained

in the apparatus at the commencement of the opera tion. When the spent-oxide becomes fairly free from sulphur, the three-way cock is placed in such a position that the liquid, in order to pass from *A* to *C*, must

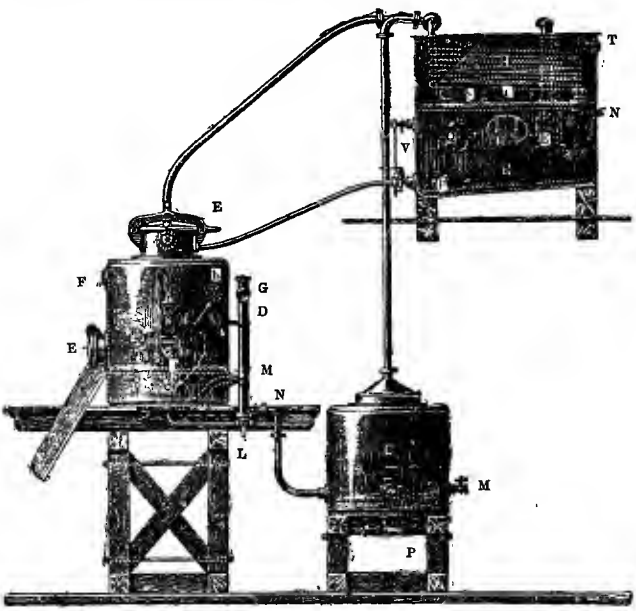


Fig. 9.

A. Extractor —B. Condenser.—C. Evaporator.—D. Regulator. —E.E.E. Manholes.—F.G. Spy-glasses.—H. Air-cock.—K. Steam inlet-valve.—L. Three-way cock.—M. Steam inlets to coils.—N. Cocks for testing purposes.—P. Cocks for emptying the vessels.—Q. Inlet for carbon bisulphide.—R. Reservoir for Solvent.—S. Inlet for condensing water.—T. Overflow pipe for condensing water.—V. Gauge-glass.

first go through the upright tube *D*. By this arrangement the level of the liquid in *A* rises to the same height as the overflow pipe in the vertical tube.

Small portions of the liquid which runs off are taken from time to time by means of a small tap provided for the purpose, and tested. When it is found to be nearly free from sulphur, the whole of the liquor is allowed to run from the extractor, the communication between *A* and *R* closed, and the carbon bisulphide distilled from *C* into *R*. The carbon bisulphide still retained by the extracted mass is driven off by live steam. As soon as the whole of the carbon bisulphide has passed off from *C*, the liquid sulphur is quickly run out into flat, four-cornered vessels, made of cast iron, where it is allowed to solidify. It contains almost invariably small quantities of carbon bisulphide. Steam cannot be employed to drive the last traces of the solvent from *C*, and care must also be taken that no water runs into *C* during the treatment of the extracted mass with steam, for if the sulphur contains moisture it solidifies on the surface, and is then only remelted with difficulty.

The mass in *A* after the treatment with steam, is raked out, and extracted with water.

The taps and valves are easily corroded by the carbon bisulphide, and to this fact most of the drawbacks and inconveniences of the process are due. On account of this corrosion leakage frequently takes place, and may cause considerable loss of the solvent. If the taps, which can only be constructed of cast iron, be well ground, frequently inspected, and smeared with graphite, this loss may be reduced to a minimum. For the purpose of caulking, it is best to use asbestos or flour-paste; oils and fats must be avoided. The losses from leakage may also be materially reduced by

taking care that during the extraction the pressure does not rise too high.

The Residues.—The residual mass, after the extraction of sulphur, ferrocyanides, and sulphocyanides, may be again employed for the purification of coal gas, provided that it is left in the form of iron oxide, and free from such impurities as lime, etc.

The residue obtained in Kunheim's process can only be used as refuse, or at best, forwarded to iron-works for use as an iron-ore. It is, therefore, an additional argument in favour of the extraction of ferrocyanides by the caustic soda process, that it yields residues having the same value as the original material.

APPENDIX.

Specific Gravity of Ammonium Sulphate Solutions at 15° C. (59° F.). (Schiff).

Specific Gravity.	Percentage $(NH_4)_2 SO_4$	Specific Gravity.	Percentage $(NH_4)_2 SO_4$	Specific Gravity.	Percentage $(NH_4)_2 SO_4$
1·0057	1	1·1035	18	1·2004	35
1·0115	2	1·1092	19	1·2060	36
1·0172	3	1·1149	20	1·2116	37
1·0230	4	1·1207	21	1·2172	38
1·0287	5	1·1265	22	1·2228	39
1·0345	6	1·1323	23	1·2284	40
1·0403	7	1·1381	24	1·2343	41
1·0460	8	1·1439	25	1·2402	42
1·0518	9	1·1496	26	1·2462	43
1·0575	10	1·1554	27	1·2522	44
1·0632	11	1·1612	28	1·2583	45
1·0690	12	1·1670	29	1·2644	46
1·0747	13	1·1724	30	1·2705	47
1·0805	14	1·1780	31	1·2766	48
1·0862	15	2·1836	32	1·2828	49
1·0920	16	1·1892	33	1·2890	50
1·0977	17	1·1948	34		

Specific Gravity of Sal-Ammoniac Solutions at 15° C. (59° F.). (Gerlach).

Specific Gravity.	Percentage $NH_4 Cl$.	Specific Gravity.	Percentage $NH_4 Cl$.	Specific Gravity.	Percentage $NH_4 Cl$.
1·00316	1	1·03081	10	1·05648	19
1·00632	2	1·03370	11	1·05929	20
1·00948	3	1·03658	12	1·06204	21
1·01264	4	1·03947	13	1·06479	22
1·01580	5	1·04325	14	1·06754	23
1·01880	6	1·04524	15	1·07029	24
1·02180	7	1·04805	16	1·07304	25
1·02481	8	1·05086	17	1·07575	26
1·02781	9	1·05367	18	1·07658	26·297

SPECIFIC GRAVITY OF CAUSTIC AMMONIA CONTAINING DIFFERENT QUANTITIES OF NH_3 TEMP. 14° C. (57° F.). (CARIUS).

Specific Gravity.	Percentage NH_3	Specific Gravity.	Percentage NH_3	Specific Gravity.	Percentage NH_3
0·8844	36·0	0·9021	28·2	0·9239	20·4
0·8848	35·8	0·9026	28·0	0·9245	20·2
0·8852	35·6	0·9031	27·8	0·9251	20·0
0·8856	35·4	0·9036	27·6	0·9257	19·8
0·8860	35·2	0·9041	27·4	0·9264	19·6
0·8864	35·0	0·9047	27·2	0·9271	19·4
0·8868	34·8	0·9052	27·0	0·9277	19·2
0·8872	34·6	0·9057	26·8	0·9283	19·0
0·8877	34·4	0·9063	26·6	0·9289	18·8
0·8881	34·2	0·9068	26·4	0·9296	18·6
0·8885	34·0	0·9073	26·2	0·9302	18·4
0·8889	33·8	0·9078	26·0	0·9308	18·2
0·8894	33·6	0·9083	25·8	0·9314	18·0
0·8898	33·4	0·9089	25·6	0·9321	17·8
0·8903	33·2	0·9094	25·4	0·9327	17·6
0·8907	33·0	0·9100	25·2	0·9333	17·4
0·8911	32·8	0·9106	25·0	0·9340	17·2
0·8916	32·6	0·9111	24·8	0·9347	17·0
0·8920	32·4	0·9116	24·6	0·9353	16·8
0·8925	32·2	0·9122	24·4	0·9360	16·6
0·8929	32·0	0·9127	24·2	0·9366	16·4
0·8934	31·8	0·9133	24·0	0·9373	16·2
0·8938	31·6	0·9139	23·8	0·9380	16·0
0·8943	31·4	0·9145	23·6	0·9386	15·8
0·8948	31·2	0·9150	23·4	0·9393	15·6
0·8953	31·0	0·9156	23·2	0·9400	15·4
0·8957	30·8	0·9162	23·0	0·9407	15·2
0·8962	30·6	0·9168	22·8	0·9414	15·0
0·8967	30·4	0·9174	22·6	0·9420	14·8
0·8971	30·2	0·9180	22·4	0·9427	14·6
0·8976	30·0	0·9185	22·2	0·9434	14·4
0·8981	29·8	0·9191	22·0	0·9441	14·2
0·8986	29·6	0·9197	21·8	0·9449	14·0
0·8991	29·4	0·9203	21·6	0·9456	13·8
0·8966	29·2	0·9209	21·4	0·9463	13·6
0·9001	29·0	0·9215	21·2	0·9470	13·4
0·9006	28·8	0·9221	21·0	0·9477	13·2
0·9011	28·6	0·9227	20·8	0·9484	13·0
0·9016	28·4	0·9233	20·6	0·9491	12·8

Specific Gravity.	Percentage NH_3	Specific Gravity.	Percentage NH_3	Specific Gravity.	Percentage NH_3
0·9498	12·6	0·9654	8·4	0·9823	4·2
0·9505	12·4	0·9662	8·2	0·9831	4·0
0·9512	12·2	0·9670	8·0	0·9839	3·8
0·9520	12·0	0·9677	7·8	0·9847	3·6
0·9527	11·8	0·9685	7·6	0·9855	3·4
0·9534	11·6	0·9693	7·4	0·9863	3·2
0·9542	11·4	0·9701	7·2	0·9873	3·0
0·9549	11·2	0·9709	7·0	0·9882	2·8
0·9556	11·0	0·9717	6·8	0·9890	2·6
0·9563	10·8	0·9725	6·6	0·9899	2·4
0·9571	10·6	0·9733	6·4	0·9907	2·2
0·9578	10·4	0·9741	6·2	0·9915	2·0
0·9586	10·2	0·9749	6·0	0·9924	1·8
0·9593	10·0	0·9757	5·8	0·9932	1·6
0·9601	9·8	0·9765	5·6	0·9941	1·4
0·9608	9·6	0·9773	5·4	0·9950	1·2
0·9616	9·4	0·9781	5·2	0·9959	1·0
0·9623	9·2	0·9790	5·0	0·9967	0·8
0·9631	9·0	0·9799	4·8	0·9975	0·6
0·9639	8·8	0·9807	4·6	0·9983	0·4
0·9647	8·6	0·9815	4·4	0·9991	0·2

Specific Gravity of Sulphuric Acid at 15° C. (59° F.) (Kolb).

Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	100 parts by weight correspond to				1 litre contains in kilos.			
			Per cent.		Percentage acid of 60° Bé.	Percentage acid of 50° Bé.	Chemically pure acid.		Acid of 60° Bé.	Acid of 50° Bé.
			SO_3	H_2SO_4			SO_3	H_2SO_4		
1·000	0	—	0·7	0·9	1·2	1·4	0·007	0 009	0·012	0·014
1·007	1	1·4	1·5	1·9	2·4	3·0	0·015	0 019	0·024	0·030
1·014	2	2·8	2·3	2·8	3·6	4·5	0·023	0·028	0·036	0·045
1·022	3	4·4	3·1	3·8	4·9	6·1	0·032	0·039	0·050	0·062
1·029	4	5·8	3·9	4·8	6·1	7·7	0·040	0·049	0·063	0·078
1·037	5	7·4	4·7	5·8	7·4	9·3	0·049	0·060	0·077	0·096
1·045	6	9·0	5·6	6·8	8·7	10·9	0·059	0·071	0·091	0·114
1·052	7	10·4	6·4	7·8	10·0	12·5	0·067	0·082	0·105	0·131

Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	100 parts by weight correspood to				1 litre contains in kilos.			
			Per cent.		Percentage acid of 60° Bé.	Percentage acid of 50° Bé.	Chemically pure acid.		Acid of 60° Bé.	Acid of 50° Bé.
			SO_3	H_2SO_4			SO_3	H_2SO_4.		
1·060	8	12·0	7·2	8·8	11·3	14·0	0·076	0·093	0·120	0·149
1·067	9	13·4	8·0	9·8	12·6	15·7	0·085	0·105	0·134	0·168
1·075	10	15·0	8·8	10·8	13·8	17·3	0·095	0·116	0·148	0·186
1·083	11	16·6	9·7	11·9	15·3	19·0	0·105	0·129	0·164	0·206
1·091	12	18·2	10·6	13·0	16·7	20·8	0·116	0·142	0·182	0·227
1·100	13	20·0	11·5	14·1	18·1	22·6	0·126	0·155	0·199	0·248
1·108	14	21·6	12·4	15·2	19·5	24·3	0·137	0·168	0·216	0·268
1·116	15	23·2	13·2	16·2	20·7	25·9	0·147	0·181	0 231	0·290
1·125	16	25·0	14·1	17·3	22·2	27·1	0·159	0·195	0·250	0·312
1·134	17	26·8	15·1	18·5	23·7	29·6	0·172	0·210	0·269	0·336
1·142	18	28·4	16·0	19·6	25·1	31·4	0·183	0·224	0·287	0·359
1·152	19	30·4	17·0	20·8	26·6	33·3	0·196	0·239	0·306	0·383
1·162	20	32·4	18·0	22·2	28·4	35·3	0·209	0·258	0·330	0·413
1·171	21	34·2	19·0	23·3	29·8	37·3	0·222	0·273	0·349	0·437
1·180	22	36·0	20·0	24·5	31·4	39·3	0·236	0·289	0·370	0·463
1·190	23	38·0	21·1	25·8	33·0	41·3	0·251	0·307	0·393	0·491
1·200	24	40·0	22·1	27·1	34·7	43·4	0·265	0·325	0·416	0·520
1·210	25	42·0	23·2	28·4	36·4	45·4	0·281	0·344	0·440	0·550
1·220	26	44·0	24·2	29·6	37·9	47·4	0·295	0·361	0·463	0·579
1·231	27	46·2	25·3	31·0	39·7	49·5	0·311	0·382	0·489	0·610
1·241	28	48·2	26·3	32·2	41·2	51·5	0·326	0·400	0·511	0·639
1·252	29	50·4	27·3	33·4	42·8	53·5	0·342	0·418	0·536	0·670
1·263	30	52·6	28·3	34·7	44·4	55·5	0·357	0·438	0·561	0·702
1·274	31	54·8	29·4	36·0	46·1	57·6	0·374	0·459	0·587	0·735
1·285	32	57·0	30·5	37·4	47·9	59·9	0·392	0·481	0·616	0·769
1·297	33	59·4	31·7	38·8	49·7	62·1	0·411	0·503	0·645	0·805
1·308	34	61·6	32·8	40·2	51·5	64·3	0·429	0·526	0·674	0·841
1·320	35	64·0	33·9	41·6	53·3	66·6	0·447	0·549	0·704	0·878
1·332	36	66·4	35·1	43·0	55·1	68·8	0·468	0·573	0·734	0·917
1·345	37	69·0	36·2	44·4	56·9	71·0	0·487	0·597	0·765	0·955
1·357	38	71·4	37·2	45·5	58·3	72·8	0·505	0·617	0·791	0·987
1·370	39	74·0	38·3	46·9	60·0	75·0	0·525	0·642	0·822	1·027
1·383	40	76·6	39·5	48·3	61·9	77·3	0·546	0·668	0·856	1·069
1·397	41	79·4	40·7	49·8	63·8	79·7	0·569	0·696	0·891	1·117
1·410	42	82·0	41·8	51·2	65·6	82·0	0·589	0·722	0·925	1·155
1·424	43	84·8	42·9	52·6	67·4	84·2	0·611	0·749	0·960	1·198
1·438	44	87·6	44·1	54·0	69·1	86·4	0·634	0·777	0·994	1·243
1·453	45	90·6	45·2	55·4	70·9	88·6	0·657	0·805	1·030	1·288

Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	100 parts by weight correspond to				1 litre contains in kilos.			
			Per cent.		Percentage acid of 60° Bé.	Percentage acid of 50° Bé.	Chemically pure acid.		Acid of 60° Bé.	Acid of 50° Bé.
			SO_3	H_2SO_4			SO_3	H_2SO_4		
1·468	46	93·6	46·4	56·9	72·9	91·0	0·681	0·835	1·070	1·336
1·483	47	96·6	47·6	58·3	74·7	93·3	0·706	0·864	1·108	1·382
1·498	48	99·6	48·7	59·6	76·3	95·4	0·730	0·893	1·143	1·429
1·514	49	102·8	49·8	61·0	78·1	97·6	0·754	0·923	1·182	1·477
1·530	50	106·0	51·0	62·5	80·0	100·0	0·780	0·956	1·224	1·530
1·540	51	108·0	52·2	64·0	82·0	102·4	0·807	0·990	1·268	1·584
1·563	52	112·6	53·5	65·5	83·9	104·8	0·836	1·024	1·311	1·638
1·580	53	116·0	54·9	67·0	85·8	107·2	0·867	1·059	1·355	1·694
1·597	54	119·4	56·0	68·6	87·8	109·7	0·894	1·095	1·402	1·752
1·615	55	123·0	57·1	70·0	89·6	112·0	0·922	1·131	1·447	1·809
1·634	56	126·8	58·4	71·6	91·7	114·6	0·954	1·170	1·499	1·872
1·652	57	130·4	59·7	73·2	93·7	117·1	0·986	1·210	1·548	1·936
1·671	58	134·2	61·0	74·7	95·7	119·5	1·019	1·248	1·599	1·996
1·691	59	139·2	62·4	76·4	97·8	122·2	1·055	1·292	1·654	2·037
1·711	60	142·2	63·8	78·1	100·0	125·0	1·092	1·336	1·711	2·118
1·732	61	146·4	65·2	79·9	102·3	127·8	1·129	1·384	1·772	2·294
1·753	62	150·6	66·7	81·7	104·6	130·7	1·169	1·434	1·838	2·284
1·774	63	154·8	68·7	84·1	107·7	134·0	1·219	1·492	1·911	2·387
1·796	64	159·2	70·6	86·5	110·8	138·0	1·268	1·554	1·990	2·416
1·819	65	163·8	73·2	89·7	114·8	143·5	1·332	1·632	2·088	2·671
1·842	66	168·6	81·6	100·0	128·0	149·4	1·523	1·842	2·358	2·872

The numbers given for 65° and 66° Bé are inexact.

Specific Gravity of Hydrochloric Acid at 15° C. (59° F.) (Kolb).

Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	100 parts by weight contain						1 litre contains in grams.					
			HCl.	Acid of 18° Bé	Acid of 19° Bé.	Acid of 20° Bé.	Acid of 21° Bé.	Acid of 22° Bé.	HCl.	Acid of 18° Bé.	Acid of 19° Bé.	Acid of 20° Bé.	Acid of 21° Bé.	Acid of 22° Bé.
1·000	0	—	0·1	0·3	0·3	0·3	0·3	0·3	1	3	3	3	3	3
1·007	1	1·4	1·5	5·3	5·0	4·7	4·4	4·2	15	53	53	47	44	42
1·014	2	2·8	2·9	10·2	9·6	9·0	8·6	8·1	29	102	96	91	87	82
1·022	3	4·4	4·5	15·8	14·9	14·1	13·3	12·6	46	164	152	144	136	129
1·029	4	5·6	5·8	20·4	19 4	18·1	17·1	16·2	60	211	199	186	176	167
1·036	5	7·2	7·3	25·7	24·2	22·8	21·5	20·4	76	267	252	236	223	211
1·044	6	8·8	8·9	31·8	39·5	27·8	26·2	24·4	93	333	308	290	274	255
1·052	7	10·2	10·4	36·6	34·5	32·6	30·7	29·1	109	384	361	343	323	306
1·060	8	12·0	12·0	42·3	39·7	37·6	35·4	33·6	127	447	421	399	375	356
1·067	9	13·4	13·4	47·2	44·3	41·9	39·5	37·5	143	503	473	447	421	400
1·075	10	15·0	15·0	52·8	49·7	46·9	44·2	42·0	161	567	533	504	475	452
1·083	11	16·6	16·5	58·0	54·6	51·6	48·7	46·2	179	630	592	559	527	500
1·091	12	18·2	18·1	63·7	59 9	56·7	53·4	50·7	197	693	652	619	583	553
1·100	13	20·0	19·9	70·0	65·9	62·3	58·7	55·7	219	771	725	685	646	613
1·108	14	21·6	21·5	75·7	71·2	67·3	63·4	60·2	238	838	788	746	702	667
1·116	15	23·2	23·1	81·3	76·4	72·3	68·1	64·7	258	904	857	807	760	721
1·125	16	25·0	24·8	87 3	82·0	77·6	73·2	69·4	279	982	923	873	824	781
1·134	17	26·8	26·6	93·6	88·0	83·3	78·5	74·5	302	1063	1000	945	890	845
1·143	18	28·6	28·4	100·0	9 1·0	89·9	83·0	79·5	325	1144	1076	1016	949	909
1·152	19	30·4	30·2	106·3	100·0	94·5	89·0	84·6	348	1225	1152	1089	1025	975
1·157	19·5	31·4	31·2	109·8	103·3	97·7	92·0	87·4	361	1271	1195	1130	1064	1011
1·161	20·0	32·2	32·0	112·6	105 9	100·0	94·4	89·6	372	1309	1231	1161	1096	1042
1·166	20·5	33·2	33·0	115·6	109·2	103·3	97·3	92·4	385	1355	1274	1204	1129	1087
1·171	21·0	34·2	33·9	119·3	112·2	106·1	100·0	94·9	397	1397	1314	1242	1171	1111
1·175	21·5	35·0	34·7	122·1	114·9	108·6	102·4	97·2	408	1436	1350	1276	1203	1140
1·180	22·0	36·0	35·7	125·7	118·2	111·7	105·3	100·0	421	1482	1394	1318	1243	1180
1·185	22·5	37·0	36·8	129·5	121·8	115·2	108·6	103·0	436	1535	1443	1365	1287	1220
1·190	23·0	38·0	37·9	133·4	125·4	118·6	111·8	106·1	451	1587	1493	1411	1330	1263
1·195	23·5	39·0	39·0	137·3	129·1	122·0	115·0	109·2	466	1640	1542	1458	1374	1305
1·199	24·0	39·8	39 8	140·2	131·7	124·6	117·4	111·4	477	1679	1579	1494	1408	1336
1·205	24·5	41 0	41·2	145·0	136·4	130·0	121·5	115·4	496	1746	1642	1567	1464	1391
1·210	25·0	42·0	42·4	149·2	140·3	132·7	125·0	119·0	513	1806	1698	1606	1513	1440
1·212	25·5	42·4	42·9	151·0	142·0	134·3	126·6	120·1	520	1830	1721	1628	1534	1456

Specific Gravity of Nitric Acid at 15° C. (59° F.). (Kolb).

Sp. Gravity.	Deg. Baumé	Deg. Tweddell.	100 parts by weight contain				1 litre contains in grams.			
			N_2O_5.	HNO_3.	Acid of 36° Bé.	Acid of 40° Bé.	N_2O_5.	HNO_3.	Acid of 36° Bé.	Acid of 40° Bé.
1·000	0	0	0·1	0·2	0·4	0·3	1	1	2	2
1·007	1	1·4	1·3	1·5	2·3	2·4	13	15	28	24
1·014	2	2·8	2·2	2·6	4·9	4·2	22	26	49	42
1·022	3	4·4	3·4	4·0	7·6	6·5	35	41	77	66
1·029	4	5·8	4·4	5·1	9·6	8·3	45	52	98	84
1·036	5	7·2	5·4	6·3	11·9	10·2	56	65	123	105
1·044	6	8·8	6·5	7·6	14·4	12·3	68	79	149	128
1·052	7	10·4	7·7	9·0	17·0	14·6	81	94	178	152
1·060	8	12·0	8·7	10·2	19·3	16·5	92	107	202	173
1·067	9	13·4	9·8	11·4	21·5	18·5	105	123	232	200
1·075	10	15·0	10·9	12·7	24·0	20·5	117	136	268	220
1·083	11	16·6	12·0	14·0	26·5	22·7	130	152	287	246
1·091	12	18·2	13·1	15·3	28·9	24·8	143	167	315	270
1·100	13	20·0	14·4	16·8	31·7	27·2	158	182	344	295
1·108	14	21·6	15·4	18·0	34·0	29·2	170	198	374	321
1·116	15	23·2	16·6	19·4	36·7	31·4	185	216	408	350
1·125	16	25·0	17·8	20·8	39·4	33·6	200	233	440	378
1·134	17	26·8	19·0	22·2	42·0	36·0	215	251	474	406
1·143	18	28·6	20·2	23·6	44·5	38·2	231	270	510	437
1·152	19	30·4	21·3	24·9	47·1	40·4	245	281	531	454
1·161	20	32·2	22·5	26·3	49·6	42·6	261	305	576	493
1·171	21	34·2	23·8	27·8	52·5	45·0	279	325	614	527
1·180	22	36·0	25·0	29·2	55·2	47·4	295	344	650	557
1·190	23	38·0	26·3	30·7	58·0	49·8	313	365	690	591
1·199	24	39·8	27·5	32·1	60·7	52·0	330	385	728	624
1·210	25	42·0	28·9	33·8	63·9	54·8	350	408	771	661
1·221	26	44·2	30·4	35·5	67·1	57·5	371	433	818	701
1·231	27	46·8	31·7	37·0	69·9	59·9	390	455	860	737
1·242	28	48·4	33·1	38·6	72·9	62·5	411	480	907	778
1·252	29	50·4	34·5	40·2	76·0	65·1	434	506	956	819
1·261	30	52·2	35·6	41·5	78·4	67·2	449	523	988	847
1·275	31	55·0	37·3	43·5	82·2	70·5	475	553	1045	896
1·286	32	57·2	38·6	45·0	85·1	72·9	496	578	1092	936
1·298	33	59·6	40·4	47·1	89·0	76·3	524	611	1154	990
1·309	34	61·8	41·7	48·6	91·9	78·7	515	635	1200	1029

Sp. Gravity.	Deg. Baumé.	Deg. Twaddell.	100 parts by weight contain				1 litre contains in grams.			
			N_2O_5.	HNO_3.	Acid of 36° Bé.	Acid of 40° Bé.	N_2O_5.	HNO_3.	Acid of 36° Bé.	Acid of 40° Bé.
1·321	35	64·2	43·5	50·7	95·8	82·1	575	670	1266	1085
1·334	36	66·8	45·3	52·9	100·0	85·7	604	704	1330	1140
1·346	37	69·2	47·1	55·0	104·0	89·1	634	739	1397	1197
1·359	38	71·8	49·1	57·3	108·3	92·7	667	777	1469	1259
1·372	39	74·4	51·2	59·6	112·6	96·5	702	818	1546	1325
1·384	40	76·8	52·9	61·7	116·6	100·0	732	853	1612	1382
1·398	41	79·6	55·3	64·5	121·9	104·5	773	901	1703	1460
1·412	42	82·4	57·9	67·5	127·6	109·4	818	954	1803	1545
1·426	43	85·2	60·5	70·6	133·4	114·4	863	1006	1903	1630
1·440	44	88·0	63·8	74·4	140·6	120·5	919	1071	2024	1735
1·454	45	90·8	67·2	78·4	148·2	127·0	977	1139	2153	1845
1·470	46	94·0	71·1	83·0	156·9	134·5	1045	1218	2302	1973
1·485	47	97·0	74·7	87·1	164·6	141·1	1109	1292	2442	2093
1·501	48	100·2	79·4	92·6	175·0	150·0	1192	1388	2623	2249
1·516	49	103·2	82·3	96·0	181·4	155·5	1247	1454	2748	2355
1·524	49·5	104·8	84·0	98·0	185·4	158·8	1280	1492	2820	2417
1·530	49·9	106·0	85·71	100·0	189·0	162·0	1311	1530	2892	2479

Strength of Caustic Soda Solution at 15° C. (59° F.).

Sp. Gr.	Baumé.	Twaddell.	Per cent. Na_2O.	Per cent. Na OH.	1 cubic metre contains in kilos	
					Na_2O.	Na OH.
1·007	1	1·4	0·47	0·61	4	6
1·014	2	2·8	0·93	1·20	9	12
1·022	3	4·4	1·55	2·00	16	21
1·029	4	5·8	2·10	2·71	22	28
1·036	5	7·2	2·60	3·35	27	35
1·045	6	9·0	3·10	4·00	32	42
1·052	7	10·4	3·60	4·64	38	49
1·060	8	12·0	4·10	5·29	43	56
1·067	9	13·4	4·55	5·87	49	63
1·075	10	15·0	5·08	6·55	55	70
1·083	11	16·6	5·67	7·31	61	79
1·091	12	18·2	6·20	8·00	68	87
1·100	13	20·0	6·73	8·68	74	95
1·108	14	21·6	7·30	9·42	81	104

Strength of Caustic Soda Solution at 15° C. (59° F.).

Sp. Gr.	Baumé.	Twaddell.	Per cent. Na_2O.	Per cent. Na OH.	1 cubic metre contains in kilos.	
					Na_2O.	Na OH.
1·116	15	23·2	7·80	10·06	87	112
1·125	16	25·0	8·50	10·97	96	123
1·134	17	26·8	9·18	11·84	104	134
1·142	18	28·4	9·80	12·64	112	144
1·152	19	30·4	10·50	13·55	121	156
1·162	20	32·4	11·14	14·37	129	167
1·171	21	34·2	11·73	15·13	137	177
1·180	22	36·0	12·33	15·91	146	188
1·190	23	38·0	13·00	16·77	155	200
1·200	24	40·0	13·70	17·67	164	212
1·210	25	42·0	14·40	18·58	174	225
1·220	26	44·0	15·18	19·58	185	239
1·231	27	46·2	15·96	20·59	196	253
1·241	28	48·2	16·76	21·42	208	266
1·252	29	50·4	17·55	22·64	220	283
1·263	30	52·6	18·35	23·67	232	299
1·274	31	54·8	19·23	24·81	245	316
1·285	32	57·0	20·00	25·80	257	332
1·297	33	59·4	20·80	26·83	270	348
1·308	34	61·6	21·55	27·80	282	364
1·320	35	64·0	22·35	28·83	295	381
1·332	36	66·4	23·20	29·93	309	399
1·345	37	69·0	24·20	31·22	326	420
1·357	38	71·4	25·17	32·47	342	441
1·370	39	74·0	26·12	33·69	359	462
1·383	40	76·6	27·10	34·96	375	483
1·397	41	79·4	28·10	36·25	392	506
1·410	42	82·0	29·05	37·47	410	528
1·424	43	84·8	30·08	38·80	428	553
1·438	44	87·6	31·00	39·99	446	575
1·453	45	90·6	32·10	41·41	466	602
1·468	46	93·6	33·20	42·83	487	629
1·483	47	96·6	34·40	44·38	510	658
1·498	48	99·6	35·70	46·15	535	691
1·514	49	102·8	36·90	47·60	559	721
1·530	50	106·0	38·00	49·02	581	750

Solubility of Sulphur in Carbon Bisulphide at 15° C. (59° F.).

Sp. gr.	Per cent S.	Sp. gr.	Per cent. S.	Sp. gr.	Per cent. S.	Sp. gr.	Per cent. S.	Sp. gr.	Per cent. S.
1·271	0	1·296	6·0	1·321	12·1	1·346	18·1	1·371	25·6
1·272	0·2	1·297	6·3	1·322	12·3	1·347	18·4	1·372	26·0
1·273	0·4	1·298	6·5	1·323	12·6	1·348	18·6	1·373	26·5
1·274	0·6	1·299	6·7	1·324	12·8	1·349	18·9	1·374	26·9
1·275	0·9	1·300	7·0	1·325	13·1	1·350	19·0	1·375	27·4
1·276	1·2	1·301	7·2	1·326	13·3	1·351	19·3	1·376	28·1
1·277	1·4	1·302	7·5	1·327	13·5	1·352	19·6	1·377	28·5
1·278	1·6	1·303	7·8	1·328	13·8	1·353	19·9	1·378	29·0
1·279	1·9	1·304	8·0	1·329	14·0	1·354	20·1	1·379	29·7
1·280	2·1	1·305	8·2	1·330	14·2	1·355	20·4	1·380	30·2
1·281	2·4	1·306	8·5	1·331	14·5	1·356	20·6	1·381	30·8
1·282	2·6	1·307	8·7	1·332	14·7	1·357	21·0	1·382	31·4
1·283	2·9	1·308	8·9	1·333	15·0	1·358	21·2	1·383	31·9
1·284	3·1	1·309	9·2	1·334	15·2	1·359	21·5	1·384	32·6
1·285	3·4	1·310	9·4	1·335	15·4	1·360	21·8	1·385	33·2
1·286	3·6	1·311	9·7	1·336	15·6	1·361	22·1	1·386	33·8
1·287	3·9	1·312	9·9	1·337	15·9	1·362	22·3	1·387	34·5
1·288	4·1	1·313	10·2	1·338	16·1	1·363	22·7	1·388	35·2
1·289	4·4	1·314	10·4	1·339	16·4	1·364	23·0	1·389	36·1
1·290	4·6	1·315	10·6	1·340	16·6	1·365	23·2	1·390	36·7
1·291	4·8	1·316	10·9	1·341	16·9	1·366	23·6	1·391	37·2
1·292	5·0	1·317	11·1	1·342	17·1	1·367	24·0	Saturated.	
1·293	5·3	1·318	11·3	1·343	17·4	1·368	24·3		
1·294	5·6	1·319	11·6	1·344	17·6	1·369	24·8		
1·295	5·8	1·320	11·8	1·345	17·9	1·370	25·1		

RECENT LITERATURE.

Lunge, G. "Coal-tar and Ammonia." 2nd Edition, 1887.

Muspratt's "Theoretical, Practical, and Analytical Chemistry."

Wanklyn, J. A. "The Gas Engineer's Chemical Manual." 2nd Edition, 1888.

Sadler, P. S. "Recovery of Tar and Ammoniacal Liquor."

Schilling, N. H. "Handbuch der Steinkohlengas-Beleuchtung."

Fleck, H. "Die Fabrikation Chem. Producte aus Thierischen Abfällen."

Stutzer, A. "Der Chilesaltpetre, seine Bedeutung und Anwendung als Düngemittel." Bearbeitet und herausgegeben von P. Wagner.

Schering. "Preparation of Pure Liquor Ammoniæ." Polytechn. Centralblatt, 1881. p. 1456.

Gerlach. "Solway's Still for Concentrating Gas-Liquor." Ing. Zeitschr. Vol. 21, p. 15.

Knublauch, O. "New Method of Determining Sulphur in Illuminating Gas." Zeitschr. Analyt. Chemie., 21, p. 335. (Abstract in Journ. Soc. Chem. Ind., 1882, p. 383.)

Feldmann, A. "Apparatus for the Distillation of Ammonia-Liquors." Dingler's Polytech. Journ., 248, p. 462. (Abstract J. S. C. I., 1883, p. 380.)

Lauber & Haussmann. "Aluminium Sulphocyanide." Dingler's Polytech. Journ. 1882, 306. (Abstract J. S. C. I., 1882, p. 364.)

Bunte. "Removal of Ammonia from Coal Gas." Dingler's Polytech. Journ. 245, p. 40. (Abstract J. S. C. I., 1882, p. 314.)

Mond, L. "Preparation of Cyanogen Compounds and Ammonia." Dingler's Polytech. Journ., 248, 366. (Abstract in J. S. C. I., 1883, p. 328.)

Tervet, R. "Ammonia from Coke." Journ. S. C. I., 1883, p. 445.

Scheurer-Kestner. "On the Destructive Distillation of Coal, and Transformation of its Nitrogen into Ammonia." Comptes Rendues, 97, p. 3. (Abstract J. S. C. I., 1883, p. 407.)

Märcker, M. "The Injurious Action of Ammonium Thiocyanate (Sulphocyanide) in Plant Growth." Biederman's Centralblatt für Agric. Chem., 12, p. 471. (Abstract J. S. C. I., 1884, p. 184.)

Cox, J. H. "Notes on Ammoniacal-Liquor." J. S. C. I., 1884, p. 158).

Otto, C., & Smith, Watson. "Manufacture of Coke with and without Recovery of Bye-Products." J. S. C. I., 1884, p. 505.

Winkler, C. "Recovery of Ammonia from Coke-oven Gases." Chemiker Zeitung, 1884, p. 691. (Abstract J. S. C. I., 1884, p. 512.)

Leidler, P. "Working up Gas-Liquor and other Products from Gas Purification." Dingler's Polytech. Journ., 252, p. 476. (Abstract J. S. C. I., 1885, p. 112.)

Wollny, E. "Crude Ammonium Superphosphate as a Manure." Biederman's Centralblatt, 1884, p. 167. (Abstract J. S. C. I., 1885, p. 126.)

James, W. "Tar and Ammonia from Blast Furnaces." Engineering, 1885, pp. 387 and 409.

Schmitz, S. "Determination of Nitrogen in Coal and Coke." Zeitschr. Anal. Chem., 25, 314. (Abstract J. S. C. I., 1886, p. 506.)

Claus's "Ammonia Process of Gas-Purification." Journ. Gas Lighting, 1886, p. 1181.

Gasch, R. "Manufacture of Sulphocyanides." Chem. Zeitung, 10, p. 274. (Abstract J. S. C. I. 1886, p. 379.)

Nafzger, F. "Manufacture of Sulphocyanides." Chem., Zeitung, 10, p. 376. Abstract J. S. C. I., 1886, p. 370.)

Wright, Lewis, T. "Notes on Gas-Liquor and Ammonia Purification." Journal of Gas Lighting, 48, pp. 280, 329, 373, 511.

Reitmair & Stutzer. "Determination of Nitrogen in Manures containing Saltpetre." Rep. Anal. Chem., 7, p. 4. (Abstract J. S. C. I., 1887, 457.)

Schmidthorn, K. "Manufacture of Ammonium Chloride and Potassium Sulphate, from Potassium Chloride and Ammonium Sulphate." Chem. Zeit., 10, p. 1499. Abstract J. S. C. I., 1887, 139.)

Schilling, E. "Nitrogen in Coals." Dingler's Polytech. Journ., 265, 218. Abstract J. S. C. I., 1887, p. 652.)

Ruffle, J. "Analysis of Ammoniated Superphosphate." J. S. C. I., 1887, p. 491.

Raupp. "Production of Ammonium Phosphate from Gas-Liquor." (Abstract J. S. C. I., 1888, p. 114.)

Wagner, Prof., "Nitrogenans Manure" (published by Whittaker).

RECENT PATENTS.

English Patent. 3208. 1870. P. Spence. Preparation of Prussian-blue from spent-oxide.

E. P. 3908. 1874. G. Valentine. Preparation of Prussian-blue from waste-products in coal-gas manufacture.

E. P. 5504. 1880. W. L. Wise (from Grouven, H.). Production of ammonium sulphate from nitrogen in coal, peat, &c.

German Patent 12,889. 1880. M. Honigmann. Stills and saturators for ammonia.

G. P. 13,395. 1880. Ströhner & Scholtz. Ammonia, &c., from coke-oven gases.

G. P. 13,429. 1880. Société anonyme des produits chemiques, des Sud-Ouest. Paris. Improvements in the apparatus for the distillation of ammoniacal liquids.

G. P. 13,594. 1880. T. Richters. Process for recovering ferrocyanides, ammonia, tar, and gas, from nitrogenous organic bodies.

G. P. 14,210. 1880. T. Richters, & L. Hagen. Purification of ammoniacal liquors, with recovery of ammonia and manures.

G. P. 15,206. 1880. T. Richters. Process for recovery of ammonia from spent-oxide before revivification.

E. P. 5173. 1880. F. J. Bolton & J. A. Wanklyn. Improvements in manufacture of artificial manures and ammoniacal products.

E. P. 1148. 1881. F. J. Bolton & J. A. Wanklyn.

Improvements in the manufacture of coal gas for illuminating purposes.

E. P. 2423. 1881. W. L. Wise, & H. Grouven. Ammonia from organic compounds.

E. P. 2709. 1882. F. J. Bolton & J. A. Wanklyn. Improvements in treatment of gas containing ammonia, for production of artificial manures, and ammoniacal salts, and in apparatus for that purpose.

G. P. 21,252. 1882. C. Schneider. Apparatus for the recovery of ammonia.

G. P. 21707. 1882. Gareis. Apparatus for distillation of ammoniacal liquids.

E. P. 433. 1882. L. Mond. Manufacture of cyanogen compounds and ammonia.

E. P. 440. 1882. G. Neilson. Extracting ammonia from furnace gases.

E. P. 3643. 1882. A. Feldmann. Improvements in the manufacture of ammonia and apparatus therefor.

E. P. 4644. 1882. C. F. Claus. Purification of coal-gas, and recovery of ammonia.

F. P. 3342. 1883. H. Kunheim & H. Zimmerman. Extraction of ferrocyanides.

E. P. 4871. 1883. H. Simon & Watson Smith. Production of ammonia and its compounds during the process of making coke or gas.

G. P. 28,137. 1883. S. Marasse. Preparation of sulphocyanides from spent-oxide.

E. P. 11,449. 1884. C. Brisons. Improvements in apparatus for distilling nitrogenous liquids.

E. P. 11,711. 1884. A. Feldmann. Improvements in the process of manufacturing ammonia.

G. P. 33,936. 1884. M. Hempel & A. Sternberg. Preparation of ferrocyanides from spent-oxide.

E. P. 381. 1885. E. W. Parnell & J. Simpson. Process for preparation of ammonia from the ammonium chloride obtained in the ammonia-soda process by heating it with alkali waste.

E. P. 2578. 1885. H. Simon. Stills for ammonia liquor.

E. P. 4902. 1885. A. Neilson & J. Snodgrass. Obtaining ammonia in connection with the distillation of oil-yielding and carbonaceous minerals.

E. P. 8973. 1885. L. Mond. Separation of ammoniacal products and tar from producer and other furnace gases.

E. P. 10,700. 1885. J. Hood. Manufacture of ammonium bichromate.

G. P. 33,320. 1885. J. Grüneberg & E. Blum. Improvements in stills for ammonia and other liquids.

E. P. 8602. 1886. J. Park. Manufacture of ammonium bichromate.

G. P. 40,215. 1886. C. Wolfrum. Process for the simultaneous treatment of gas-liquor and spent-oxide.

E. P. 970. 1887. E. W. Parnell & J. Simpson. Improvements in the treatment of ammonium sulphide solutions with carbonic acid gas for the purpose of obtaining ammonium carbonate and strong sulphuretted hydrogen.

E. P. 17,050. 1887. Manufacture of ammonium sulphite.

INDEX.

A.

ACID ammonium carbonate, 14, 72.
Amido-salts, 9.
Ammonia :—
Composition and properties, 1.
Estimation of, 20, 23.
Occurrences and formation, 3.
Solubility in water, 8.
Sp. gr. of solutions, 112.
Ammonium alum, 11, 54.
„ bichromate, 19, 79.
„ carbamate, 15, 71.
„ carbonate, 13, 70.
„ chloride (*see* sal-ammoniac).
„ chromate, 18, 79.
„ cyanide, 19.
„ hyposulphite, 19.
„ metavanadate, 18, 82.
„ molybdate, 18.
„ nitrate, 16, 73.
„ oxalate, 17, 81.
„ phosphate, 16, 77.
„ sulphate, 10, 39.
„ „ Analysis of, 51.
„ „ Applications, 52.
„ „ Imports into Germany, 53.
„ „ Relative value as manure, 52.
„ „ Sp. gr. of solutions, 111.
„ sulphide, 15, 81.
„ sulphocyanide, 16, 75, 98.
„ superphosphate, 78.
„ thiocarbonate, 17.
„ thiocyanate, 16, 75, 98.
„ thiosulphate, 19.
Azotometer, 23.

B.

BARIUM thiocyanate or sulphocyanide, 100.
Bog-iron ore, 87.
Bolton and Wanklyn's gas-purification process, 78.
Buff and Dunlop's extraction apparatus, 98.

C.

CANARINE, 77.
Caustic ammonia, 8, 55.
„ „ sp. gr. of different strengths, 112.
Caustic soda:—
Normal solution of, 26.
Sp. gr. of solutions, 118.
Chloride of nitrogen, 9.
Chili-saltpetre, 52.
Coal, percentage of nitrogen in, 6.
Concentrated gas-liquor, 62.
Crude caustic ammonia, 63.
Cuprammonium sulphate, 12, 54.

D.

DENSIMETER, 30.
Dephlegmator, 55, 56.
Distillation method of estimating ammonia, 20.
Dry distillation of coal, 5.
„ „ bones, 8.

E.

EVAPORATORS, 65.
Extractors, 98, 107.

F.

FELDMANN'S still, 43.
Ferrocyanides, 90, 95, 101.
Ferrous ammonium sulphate, 11, 53.

G.

GAS-LIQUOR:—
Analysis, 30, 32.
Carriage and storage, 33.
Composition, 28.
Formation, 7.
Removal of ammonium sulphide from, 34
Grüneberg and Blum's still, 45.

H.

HYDROCHLORIC acid, 38.
„ „ sp. gr. of solutions, 116.
Hydrometer, 30.

L.

LAMING'S mixture, 86.
Laughing-gas, 16, 75.
Lime, 38.
Lime-mud, 84.
Literature, 121.
Liquor-ammoniæ, 8, 55.
„ „ fortior, 61.

M.

METHYL-ORANGE solution, 27.

N.

NESSLER's reagent, 27.
Nickel ammonium sulphate, 11, 54.
Nitric acid, 38.
„ „ sp. gr. of solutions, 117.
Nitrogen compounds in coal-tar products, 91.
Normal sulphuric acid solution, 26.
„ caustic soda solution, 26.

O.

OXAMIC acid, 18.
Oxamide, 18.

P.

PATENTS, 124.
Prussian-blue, 90, 96.
„ „ volumetric estimation of, 97.

R.

RECENT literature, 121.
„ patents, 124.
Residues from spent-oxide, 110.
Revivification of spent-oxide, 92.

S.

SAL-AMMONIAC, 12, 64.
„ „ applications, 69.
„ „ sp. gr. of solutions, 111.
„ „ sublimation, 68.
Saturators, 47, 65.
Sodium ferrocyanide, 104.
„ hypobromite solution, 27.
Spent-oxide :—
Analysis of, 94.
Composition of, 91.
Separation of nitrogen compounds in, 89.
Separation of sulphur in, 86.
Revivification of, 92.
Standard solutions, preparation of, 25.
Stills for ammonia, 40, 41, 43, 45, 56.
Sulphur :—
Extraction from spent-oxide, 89, 105.
„ „ gas-liquor, 89.
„ „ waste-gases, 83.
Solubility in carbon bisulphide, 120.
Sulphuric acid, 35.
„ „ analysis of, 36.
„ „ sp. gr. of solutions, 113.
„ „ transport and storage, 37.

T.

TINCTURE of litmus, 27.

V.

VOLATILE liver of sulphur, 15.

W.

WASTE-GASES, 82.
„ „ sulphur from, 83.
Waste-liquor, 84.
„ „ clarification of, 85.

JOHN J. GRIFFIN & SONS, LTD.,

CHEMICAL & PHILOSOPHICAL INSTRUMENT MAKERS

AND LABORATORY FURNISHERS,

22, Garrick Street, Covent Garden, London, W.C.,

SUPPLY THE

APPARATUS

MENTIONED IN

WINKLER'S TECHNICAL GAS ANALYSIS,

TRANSLATED BY LUNGE.

Wanklyn's Gas Engineer's Chemical Manual.

THE ALKALI MAKER'S POCKET BOOK,

By DRS. LUNGE and HURTER.

THE GAS REFEREES' APPARATUS.

AND EVERY DESCRIPTION OF

APPARATUS AND FINE CHEMICALS

USED BY GAS ANALYSTS.

ILLUSTRATED CATALOGUES OF

CHEMICAL APPARATUS, | PHYSICAL APPARATUS,
ELECTRICAL ,, | PHOTOGRAPHIC ,,

Post Free upon application.

JOHN J. GRIFFIN & SONS, LTD.,

22, GARRICK STREET, COVENT GARDEN, LONDON, W.C.

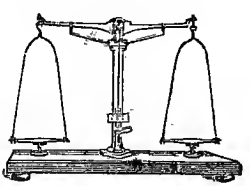
ESTABLISHED 1875.

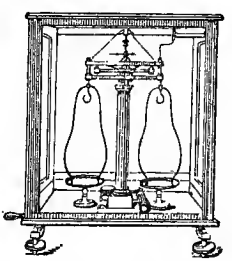
OTTO WOLTERS,

55, Upper Marylebone St., Portland Place, London, W.

MANUFACTURER OF

CHEMICAL BALANCES.





SPECIALITY:

WOLTERS' CELEBRATED SHORT-BEAMED ANALYTICAL BALANCES,

For Chemical Analysis, and for all Extreme Weighing.

THE MOST SENSITIVE AND IN EVERY RESPECT MOST PERFECT BALANCE EVER CONSTRUCTED.

This Balance, which I have introduced into this Country, is supplied by me to the Government, and to a great number of the leading Institutions.

Price of Balances which are most in use in the Laboratory:

Balance to carry 200 Gramme, £15 15s.
„ „ 500 „ £19 19s.

Maker of Mr. Halse's Sugar Balance; also maker of Specific Gravity Balances and Instruments.

INFORMATION ON APPLICATION.

LONDON
PRINTED BY GILBERT AND RIVINGTON, LIMITED,
ST. JOHN'S HOUSE, CLERKENWELL ROAD.

8vo, 740 pages, with 191 Working Drawings to Scale, £1 11s. 6d.

COAL-TAR & AMMONIA,

Being the Second and Enlarged Edition of "A Treatise on the Distillation of Coal Tar and Ammoniacal Liquor."

BY

GEORGE LUNGE, Ph.D.,

Professor of Technical Chemistry in the Federal Polytechnic School, Zurich, &c.

"Several new chapters have been added, embracing the recovery of Coal-Tar and Ammonia from other sources than the manufacture of illuminating gas, the burning of tar as fuel, &c.; others have been completely re-written; and few pages have been taken unchanged from the former edition—so that this is to all intents and purposes a new book. It has been about doubled in size, both as regards letter-press and illustrations."—*Journal of Gas Lighting.*

3 Volumes, 8vo, with more than 700 Illustrations drawn to Scale, £4 16s.

SULPHURIC ACID & ALKALI MANUFACTURE,

A THEORETICAL AND PRACTICAL TREATISE ON.

By Professor GEORGE LUNGE, Ph.D., &c.,

Formerly Manager of the Tyne Alkali Works, South Shields.

"To the best of our knowledge it is the most complete, practical, and thorough-going treatise on the subject to be met with in any language."—*Chemical News.*

GURNEY & JACKSON, 1, PATERNOSTER ROW, LONDON

(Successors to Mr. VAN VOORST).

A LIST

OF

IMPORTANT WORKS

ON THE

MANUFACTURING INDUSTRIES

CAN BE HAD OF

SAMPSON LOW, MARSTON, SEARLE, & RIVINGTON, Ltd.,

ST. DUNSTAN'S HOUSE, FETTER LANE, LONDON.

C. & W. WALKER,

Chemical Engineers.

C. & W. WALKER'S PATENT SULPHATE OF AMMONIA APPARATUS, unequalled for simplicity, economy, and remarkable efficiency.

CLAUS' PATENT SULPHUR RECOVERY PLANT for extracting pure Sulphur from the waste gases of Saturator of Sulphate Plant, and destroying all noxious fumes.

MIDLAND IRON WORKS, DONNINGTON, NEAR NEWPORT, SALOP.

8, FINSBURY CIRCUS, LONDON, E.C.

WILLIAM METCALF,

MANUFACTURER OF

NAPHTHA, PREPARED OIL, PARANAPHTHALINE,

BRICK-PRESS OIL, POT OIL, DIPPING OILS,

Creosote for Preserving Timber, Black Varnish, Pitch, Asphalt, Carbolic Oil, Corfe Oil, &c., &c.,

SHEFFIELD TAR WORKS, WASHFORD ROAD, ATTERCLIFFE, SHEFFIELD;

And at CHURCH, near ACCRINGTON, LANCASHIRE.

TAR AND LIQUOR PURCHASED.

Sulphate of Ammonia Plant.

Messrs. Cutler are now giving special attention to this Apparatus. They have recently most successfully erected at Dublin a Plant = 120 tons per day, and are prepared to supply the **very best Plant** on most favourable terms.

Messrs. Cutler make a speciality of **Gas Work Plant,** and have constructed Gasholder and all other description of Gas **Apparatus of** the very **largest dimensions,** both at home and abroad. They have now in hand for the Imperial Continental Gas Association at Vienna, a Treble Lift Holder **200 ft. dia. × 123 ft. high, the largest on the Continent of Europe.**

Messrs. Cutler manufacture, amongst others, the following specialities :—

Cutler's Patent Guide Framing for Gasholders.
Cutler's Patent Freezing Preventer for Gasholder Cups.
Cutler's Improved Sight Boxes for Retort Bench Flues.
Cutler's Patent Mouthpiece Supports, to relieve Retorts of weight of Mouthpieces.
Cutler's Patent Removable Seal, to remove pressure from Retorts.
Livesey & Tanner's Patent Differential Tar and Liquor Overflows.
Brett's Patent Coke Barrow.
Richmond's Patent Coke Barrow.
Wate's Patent Combined Shoot and Platform.
Morris & Cutler's Patent "Perfect Condenser."
Cutler's Patent "Simplex Distributer."
Cutler's Improved Jet Distributer.
Cutler's Patent Water Valves for Purifiers, &c.
Cutler's Patent Iron Sieves for Lime Purifiers.
Church's Patent Wood Sieves, very light and durable.
Cutler's Patent Top Sheeting for Gasholders.
Cutler's Patent Adjustable Outlet for Tar and Liquor Tanks.
Dougall & Cutler's Patent Furnace Frame and Doors.

SAMᴸ. CUTLER & SONS, Engineers, &c.

Works:
PROVIDENCE IRONWORKS,
MILLWALL, E.

Offices:
16, GT. GEORGE STREET,
WESTMINSTER, S.W.